SFUND RECORDS CTR
2120963

WASTE DISPOSAL INC. SUPERFUND SITE

Project Coordinator

November 17, 1997 Project No. 94-256

Ms. Andria Benner
U.S. Environmental Protection Agency
75 Hawthorne Street, No. H-7-2
San Francisco, California 94105-3901

Transmittal
Appendix A - Revised Supplemental Field Sampling and Analysis Plan (Rev. 2.0),
Appendix B - Revised Supplemental Quality Assurance Project Plan (Rev. 2.0)
and Treatability Study Workplan (Appendix C of the RD Investigative Activities Workplan)
Waste Disposal, Inc. Superfund Site
Santa Fe Springs, California

Dear Ms. Benner:

Enclosed please find five copies of the following appendices to the Treatability Study Workplan:

- Appendix A - Revised Supplemental Field Sampling and Analysis Plan (Rev. 2.0)
- Appendix B - Revised Supplemental Quality Assurance Project Plan (Rev. 2.0)

This submittal is pursuant to the requirements of our recent telephone conversations and your letter dated November 14, 1997. Table 1, Responses to November 14, 1997 Comments, is attached. Attachments B.1 and B.2 to the Revised Supplemental Quality Assurance Project Plan will be submitted under separate cover on November 19, 1997, per our previous arrangement.

We are prepared to resume field activities on Monday, November 24, 1997. Additionally, we understand that EPA will perform audits of both field and laboratory activities.

Please call me at (714) 577-2955 or Roberto Puga of TRC at (714) 727-9336 if you have any questions or comments.

Sincerely,

Roberto Puga for
Ian A. Webster
WDIG Project Coordinator

IAW/ML:ks
Enclosures

cc: James Barton, COE
Keith Elliott, RWQCB
Shawn Haddad, DTSC
Pat Hotra, SCAQMD
Andy Lazzaretto, City of Santa Fe Springs
Virginia Maloles, LA County DOHS
Neal Navarro, COE
Shelby Moore, Esq., WDIG
Bill Nelson, ATSDR
Darryl Petker, CIWMB
Roberto Puga, TRC
Stan Smucker, Ph.D., EPA
Kathy Steuer, Esq., EPA, ORC
Dave Taylor, EPA
Marilyn Underwood, Ph.D., CDM Federal
John Wondolleck, CDM Federal
WDIG Members

TABLE 1

RESPONSES TO NOVEMBER 14, 1997 EPA COMMENTS TO REVISED SUPPLEMENTAL FSAP AND QAPP WASTE DISPOSAL, INC. SUPERFUND SITE

EPA CONCERN/COMMENT	RESPONSE TO COMMENT
Concerns:	
4. (September 19, 1997) **[Section C.3.3, Predesign Data] *It should be defined how soil* permeability will be determined. It is recommended that a gas tracer test be used to help establish permeability criteria (due to expected soil heterogeneity and construction debris).** (November 5, 1997) **This comment has not been addressed. Sampling and analysis methods must be included in the SAP and QAPP. The SAP and QAPP must demonstrate that the samples collected for permeability testing are representative, and the method selected is appropriate.** This concern has been partially addressed. The response to comments states "permeability tests (will be) performed using API-Method RD-40." However, this statement has not been formally added to the workplan. Additionally, details of how this method will be performed and a copy of the method should be included with the FSP and the QAPP. The response to comments also states "geotechnical methods are not required to be included in sampling and analysis plans." Geotechnical methods should be included in sampling and analysis plans, especially for parameters such as permeability testing that can be determined by a variety of methods with the resultant data used make critical site decisions.	1. Additional details describing the air permeability test have been added to Section A.5.1.2. A copy of Method API-RP-40 is included as Attachment A.2 of the Revised Supplemental FSAP.
Additional Comments [November 5, 1997]:	
1. **[Treatability Study Workplan (TSW) Table A.2 (Included as an amendment to the Field Sampling and Analysis Plan Table A.2.), DQO Development Process] There are several deficiencies in the DQO development process that are reflected in this table.** A. **[General] Table A.2 of the "Treatability Study Workplan" should be combined with Table A.1 of the "Revised Supplemental FSAP." Additionally, DQO development information should be included for ambient air, sump solids and sump liquids.** This concern has been partially addressed. Table A.1 was revised to include sump material and included with the response to comments, however a revised Table A.2 was not included.	1. A description of the DQO development process has been added to Table A.2.

TABLE 1

RESPONSES TO NOVEMBER 14, 1997 EPA COMMENTS TO REVISED SUPPLEMENTAL FSAP AND QAPP WASTE DISPOSAL, INC. SUPERFUND SITE (Continued)

EPA CONCERN/COMMENT	RESPONSE TO COMMENT
Additional Comments [November 5, 1997] (Continued)	
B. [Intended Data Use] The intended data use for Reservoir Liquids Monitoring should be expanded to include "information to aid in remedial design and characterization for evaluation of possible disposal options." The intended data use for SVE Monitoring should be expanded to include "monitoring for emissions characterization and compliance." This concern has been partially addressed. Table A.1 was revised and included with the response to comments, however a revised Table A.2 was not included.	1. A description of the DQO development process has been added to Table A.2.
***D. [Required Analytical Methods of DQO Levels]* Levels of Concern and Compounds of Concern should be identified for all data uses. Without this *information DQO's cannot be fully* developed and the applicability of the methods selected cannot be fully evaluated. It is recommended that the *levels of concern stated in* EPA's "Subsurface Gas Contingency Plan," Table 7, for VOCs (Volatile Organic Compounds), California Maximum Contaminant Levels (MCLs) and other regulatory requirements be used.** This concern has been partially addressed. The response to comment states "Table A.1 will be revised to reflect that the compounds of concern and their levels as stated in EPA's "Subsurface Gas Contingency Plan", however the plan has not been updated to include these Compounds of Concern. Additionally, Compounds of Concern need to be identified for the non-VOA analytical methods requested and Levels of Concern must be identified for all Compounds of Concern.	1. Table B.1 provides a summary of the Compounds of Concern. A discussion of the DQO process is presented in Table A.2. Table A.1 provides a list of the relevant requirements which were used to *establish the detection limits for these constituents.*

TRC

TABLE 1

RESPONSES TO NOVEMBER 14, 1997
EPA COMMENTS TO
REVISED SUPPLEMENTAL FSAP AND QAPP
WASTE DISPOSAL, INC. SUPERFUND SITE
(Continued)

EPA CONCERN/COMMENT	RESPONSE TO COMMENT
Additional Comments [November 5, 1997] (Continued)	
G. **[Required analytical Methods of DQO Levels] SW-846 Method 8080 is not applicable for certain samples with high levels of matrix interferences. There is reason to suspect that this method may not be appropriate for the reservoir liquid samples and the solid samples. Please analyze these samples for Polychlorinated Biphenyls (PCBs) by EPA SW-846 Method 8082 with extract cleanup by Method 3665A, instead of Method 8080 for the full pesticide list (for these two matrices only).** This comment has been partially addressed. The response to comments states "If matrix interferences are detected .... PCB's will be analyzed for using EPA Method 3665A and EPA Method 8082." This response is acceptable, however this criteria should be formally included in the plan. Additionally, Levels of Concern should be incorporated into this decision making process.	1. Section A.4.3 of the Revised Supplemental FSAP has been revised to indicate that if EPA Method 8080 does not achieve the required QA/QC limits for PCB's (i.e., matrix spite recovery levels). The PCB's will be analyzed for using EPA Methods 3665A and 8082. 2. Table A.1 provides a list of the relevant requirements which were used to establish the detection limits for the PCBs.
2. **[Revised Supplemental Field Sampling and Analysis Plan Section A.3.2, Soil Sampling] This Section does not accurately describe how Method 5035 will be implemented. Please review Section 6.2 of Method 5035. All solid samples should be collected using the methanol field preservation method for high level analysis.** This concern has been satisfactory addressed. An acceptable procedure for implementation of EPA Method 5035 has been included in Section A.3.2.	1. No response required.
Additional Comments:	
1. [General] Conditional approval of this plan for the soil/sump sampling event is contingent on the EPA QA Program conducting a project specific laboratory audit of the laboratory used to analyze samples from this event. Additionally, the laboratory Standard Operation Procedures for the methods requested and the laboratory Quality Assurance Plan should be received by the QA Program on or before November 19, 1997.	1. As indicated in the cover letter, an audit of VOC Analytical will be conducted by EPA on December 4, 1997. A copy of VOC Analytical's relevant QA/QC documentation will be forwarded to EPA on or before November 19, 1997.
2. [General, Sampling Locations] Decision criteria for the selection of sampling locations needs to be included in this plan.	1. A discussion of the sample location selection criteria has been added to Section A.3.

TRC *Environmental Solutions Inc.*

APPENDIX A
REVISED SUPPLEMENTAL FIELD SAMPLING AND ANALYSIS PLAN

(Rev 2.0)

WASTE DISPOSAL, INC.
SUPERFUND SITE
SANTA FE SPRINGS, CALIFORNIA

Prepared for

United States Environmental Protection Agency

Prepared by

Waste Disposal Inc., Group (WDIG)

Project No. 94-256
November1997

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

APPENDIX A
REVISED SUPPLEMENTAL FIELD SAMPLING AND ANALYSIS PLAN

A.1 INTRODUCTION

1. This Revised Supplemental Field Sampling and Analysis Plan (FSAP) has been prepared to support field activities of the Treatability Study Workplan (Treatability Workplan) for the Waste Disposal, Inc. (WDI) Superfund site in Santa Fe Springs, California. This FSAP is Appendix A to the Treatability Workplan. A Revised Supplemental Quality Assurance Project Plan (QAPP), has been prepared separately as Appendix B to the Treatability Workplan.

2. Since this Revised Supplemental FSAP is an appendix to the Treatability Workplan, project descriptions and project organization chapters are not repeated here. Standard Operating Procedures (SOPs) for various elements of the work are included as Attachments to the RD Investigative Activities Workplan Revised QAPP.

3. Modifications to this Revised Supplemental FSAP may be required whenever the Treatability Workplan is modified or to suit conditions encountered as the work progresses. The primary procedure for making a modification to the Workplan will be through the use of a Technical Memorandum (TM), as described in Section 4.2.1 of the RD Investigative Activities Workplan. In the event a modification is required, a TM will be submitted describing the proposed modification and the appropriate SOPs for required sampling activities, if different from those described herein and included in Attachment B.3 of the Revised RD Investigative Activities Workplan QAPP. On approval of the modifications, revised pages, tables or figures as appropriate will be submitted to EPA.

4. This appendix is organized as follows:
    - Section A.2 - Sampling Objectives
    - Section A.3 - Rationale for Sampling
    - Section A.4 - Analysis Requirements
    - Section A.5 - Methods and Procedures

A.2 SAMPLING OBJECTIVES

1. The primary purpose of the proposed soil sampling and analysis program is to obtain additional information to complete the Remedial Design.

2. The specific objectives of the proposed sampling include:
   - Chemical Analysis of Soil and Sump Materials
     - Identification and quantification of constituents of concern in areas not previously evaluated or in areas where additional data is needed to complete the remedial design.
     - Identification and quantification of constituents of concern in areas near occupied buildings which may be relevant to risk evaluations.
   - Geotechnical Analysis of Soils and Sump Materials
     - Evaluation of geotechnical properties (i.e., moisture, density and grainsize) for RD.
     - Evaluation of permeability and soil characteristics to determine the applicability of soil vapor extraction.

3. Table A.1 summarizes the Data Quality Objectives (DQOs) for the various site media. Table A.2 provides a description of the DQO process for the proposed soil and sump material sampling and analysis. DQOs are discussed in more detail in Section B.4 of the Revised Supplemental QAPP (Appendix B).

A.3 RATIONALE FOR SAMPLING

A.3.1 APPROACH

1. As outlined in the Treatability Workplan, the primary purpose of the field investigation activities is to refine site characterization data as required to complete the Remedial Design (RD). The primary field sampling activities to be completed during the Treatability Study will be the collection and analysis of subsurface soil samples from the areas indicated in Figure A.1. The samples collected from these areas will be analyzed for VOCs, SVOCs, pesticides petroleum hydocarbons and metals. Samples will be tested using TCLP and CamWet Extraction methods, for evaluation of hazardous waste criteria. In addition, selected samples will be collected and tested for geotechnical purposes, as part of this sampling.

2. Areas for chemical and geotechnical analysis will be selected based on the following criteria:
   - Locations where liquids were discovered to be perched on top of sump material.
   - Preprecipitative areas of the sump material.
   - Sump material adjacent to onsite buildings.
   - Other areas identified by EPA of potentially continuing free product liquids.

   However, due to the dynamic nature of the field investigation, this sampling plan may be revised in the field on approval by EPA.

3. The sampling efforts to be used in support of these field activities will incorporate the following strategies:
   - Follow appropriate protocols in the Health and Safety Plan to minimize exposure to potentially contaminated media.
   - Follow labeling protocols for each sample collected. Detailed protocols are provided in the Revised Supplemental QAPP (Appendix B).
   - Place samples in laboratory-certified clean receptacles.
   - Adhere to field sample collection and handling procedures as described herein, and supported by Quality Control (QC) measures provided in the Revised Supplemental QAPP.
   - Follow sample packaging and Chain-of-Custody protocols to assure that samples which may be analyzed are delivered to the laboratory and stored appropriately. Detailed protocols are provided in the Revised Supplemental QAPP.

4. EPA will be notified not less than 14 days in advance of sample collection activity.

A.3.2 SOIL SAMPLING

1. Soil samples will be collected using a Geoprobe type, hydraulically pushed boring system. Samples will be collected using a 1.5-inch diameter cylinder, equipped with a polyacrylate inner sleeve.

2. Soil samples selected for analysis will be collected from the polyacrylate Geoprobe sleeve, immediately upon retrieval from the subsurface and placed into an unpreserved vial, as per section 2.2.1 of EPA Method 5035 for high level samples. Method 5035 is provided in Attachment A.1. A portion of this sample will then be accurately weighed into the premade preserved vial for analysis as per section 6.2 of Method 5035. Soil samples will be analyzed

using EPA Method 5035 (closed system purge and trap extraction for VOCs in soils and waste samples). This sampling method consists of the following elements:

- Retrieval of samples.
- Field extraction of samples using methanol (EPA Method 5035).
- Laboratory completion of extraction and analysis using purge and trap procedures.

A copy of EPA Method 5035 is provided in the Appendix B, Attachment B.3, as SOP O.

A.4 ANALYSIS REQUIREMENTS

A.4.1 REQUEST FOR ANALYSIS

1. Soil sampling at the WDI site (CERCLIS Number CAD 980884357) is anticipated to occur in November 1997 or as soon as the Revised Support FSAP and QAPP are approved. The laboratory analyses to be performed for the WDI Treatability Study will consist of only Routine Analytical Services (RAS). The selected laboratory will be requested to conform with the Contract Laboratory Program Inorganic and Organic Statements of Work, in performing the analyses. Table B.1 of the Revised Supplemental QAPP provides a summary of the analytical procedures for soil samples, including the analytical quality assurance (QA) control limits, and the detection limits for each parameter. Approximately 10 to 15 soil samples will be collected and analyzed for total RAS metals, volatile organics, semivolatile organics, PCBs and pesticides, although this range may be increased due to field observations.

A.4.2 MONITORING/TESTING FREQUENCIES

A.4.2.1 Soil Samples

1. Soil samples will be collected on a one-time basis only from the locations indicated in Figure A.1. If additional locations or samples need to be sampled, a TM will be submitted to EPA for approval, indicating the need and rationale for collecting additional data.

A.4.3 ANALYTICAL PROCEDURES

1. Procedures for analyses of subsurface soil samples are presented in the Revised Supplemental QAPP (Appendix B). A summary of the methods to be used is provided in Table A.3.

2. If during these analysis of the samples for Pesticides and PCB's (EPA Method 8080), the matrix Spike Recovery Levels are below the QA/QC criteria, EPA Method 3665A and 8080 will be used for the PCB analysis.

A.4.4 ANALYTICAL PARAMETERS, SAMPLE CONTAINERS, METHODS OF PRESERVATION, AND HOLDING TIMES

1. Information on analytical parameters, sample containers, methods of preservation, and holding times are presented in Table B.1 of the Revised Supplemental QAPP.

2. Table B.2 of the Revised QAPP provides a list of the Quality Control Samples to be collected and their respective frequencies.

A.5 METHODS AND PROCEDURES

A.5.1 SAMPLE COLLECTION

A.5.1.1 Introduction

1. The following sections describe the field sample collection methods and procedures that will be implemented during investigations at the site.

A.5.1.2 Subsurface Soil Samples

A.5.1.2.1 Subsurface Soil Sampling Locations and Underground Utility Clearance

1. Prior to the commencement of drilling activities, the locations of the proposed vapor wells will be marked with wooden stakes as measured from a definable site feature for easy conversion to site plans and figures. If this procedure proves to be too difficult or the accuracy is not adequate, then a survey crew may be procured. An inspection by personnel with knowledge of underground utilities and lines (e.g., Dig Alert) will be conducted, at which time each borehole without location interferences will be given a "clearance" by marking (flagging) the stake with yellow tape.

2. Drilling may only be performed at the "cleared" staked locations. If areas are deemed questionable by inspection personnel, the vapor well will be moved to the nearest location which can be cleared. In the unanticipated event that an essential vapor well cannot be cleared, a geophysical survey or other pipeline locator method may be performed to locate potential utilities and lines. However, since geophysical methods may not be able to detect utility lines lacking ferrous (iron) elements, vapor wells proposed in this area would also require clearance by checking the area using hand augering techniques.

A.5.1.2.2 Borehole Drilling for Subsurface Soils

1. The primary method for subsurface soil sampling will be the use of a Geoprobe type hydraulically pushed boring system (HPBs) using a polyacrylate inner sleeve. During soil sampling, the soils will be evaluated and logged as indicated in SOP A (RD Investigative Activities Workplan, Appendix B) for soil type and soil characteristics.

2. Borehole cuttings will be disposed pursuant to the procedures described in Section A.5.3.

A.5.1.2.3 Sampling

1. Soil samples will be collected using a Geoprobe type, hydraulically pushed boring system. Samples for VOC analysis will be collected from the Geoprobe polyacrylate tube using an EnCore™ sampler or equivalent, as per EPA Method 5035. The VOC samples will then be prepared and handled as indicated in Method 5035.

2. Samples for SVOC, pesticides, PCB's, petroleum hydrocarbons and metals analysis will be collected by the laboratory from a sealed polyacrylate tube.

3. Samples for permeability testing will be collected in the Geoprobe polyacrylate tubes. After withdrawal from the soil, the tube will be capped and taped closed. The selected area or zone for testing will be marked on the tube and indicated on the chain of custody. The tube will then be transported to the laboratory for testing, as per API-Method-RP-40. API-Method-RP-40 is provided in Attachment A.2.

A.5.2 DECONTAMINATION

A.5.2.1 <u>Equipment Decontamination</u>

1. Augers flights (including hand augers and HPB units) will be decontaminated prior to and between drilling at each borehole site by steam cleaning or high pressure hot water cleaning. Equipment decontamination procedures are described in detail in Appendix B.3, SOP G of the Revised RD Investigative Activities Workplan.

2. The HPB rig may be decontaminated at anytime during the sampling program, if the field geologist or engineer believes the integrity of soil borings may be affected by contaminated conditions on the rig. Decontamination will consist of steam cleaning or high-pressure washing of truck wheels, chassis, or other rig components affected.

3. Nondisposable sampling equipment (e.g., stainless steel bailer) will be decontaminated at a central location where it was used. Decontamination fluids will be collected for proper disposal.

4. The following is the general decontamination procedure for field equipment used in the subsurface investigation.

   - Removal of soil and placement in drum.
   - Washing and scrubbing with nonphosphate detergent.
   - Tap water rinse.
   - 0.1N nitric acid rinse (when cross contamination from metals is a concern).
   - Deionized/distilled water rinse (when semivolatile organic compounds [SVOCs] and non-SVOC contamination may be present).
   - Isopropyl alcohol rinse.
   - Deionized/distilled water rinse.
   - Organic-free water rinse.
   - Air dry.
   - Wrapping in aluminum foil, shiny side out, for transport.

A.5.3 DISPOSAL OF SOIL CUTTINGS, PURGED GROUND WATER, AND ASSOCIATED SAMPLING WASTES

1. Soil cuttings, purge ground water and associated wastes will be managed as indicated in Section A.5.3 of the RD Investigation Activities FSAP (Appendix A).

A.5.4 SAMPLE CONTAINERS

1. Table B.1 of the Revised Supplemental QAPP lists the sample container requirements appropriate for the analytical procedures.

2. Each sample container will be labeled with the name of the person taking the sample, sample date and time, sample identification code, sample type, preservation method and analyses to be performed. The label will also indicate if the sample is to be held in appropriate storage by the laboratory until the geologist/engineer determines if analyses are to be performed based on initial analytical results for representative samples.

A.5.5 SAMPLE PRESERVATION

1. Appropriate sample containers and preservatives for soil samples will be supplied by the analytical laboratory or equivalent reputable source. A listing of these containers, preservation methods, and associated holding times are provided in Table B.1 of the Revised Supplemental QAPP (Appendix B).

A.5.6 SAMPLE SHIPMENT

1. The samples will be packed in the following manner for shipment. Detailed sample transportation procedures are described in SOP H of the RD Investigative Activities Workplan Appendix B.3.

A.5.7 SAMPLE DOCUMENTATION

A.5.7.1 Sample Identification

1. Each sample collected will be identified as having originated from the site by prefacing each sample designation with "WDI," for Waste Disposal, Inc. Each sample will be further identified using the sample designation "TS" for Treatability Study, as indicated below.

A.5.7.2 Sample Location, Depth and Identification

1. Each sample collected will be identified by an alpha and numerical code, corresponding to the sample media and number, as illustrated below:
    - WDI TS-01-05 - Treatability Study Sample 1 at 5 feet.
    - WDI TS-02-10 - Treatability Study Sample 2 at 10 feet.

A.5.7.3 Chain-of-Custody

1. Chain-of-Custody procedures are discussed in Section B.4 of the Revised Supplemental QAPP which will be used to maintain and document sample possession.

A.5.7.4 Field Notebook

1. In the field, the Field Engineer/Geologist collecting the samples will record the appropriate portions of the following information for each sample collected, as appropriate for the sample type, using indelible ink, in a field logbook or on a field data sheet.

2. Detailed field documentation procedures are presented in Appendix B.3, SOP J of the RD Investigative Activities Workplan.

TABLE A.1

DQO DEVELOPMENT PROCESS
WASTE DISPOSAL, INC.

ACTIVITY	SUBSURFACE SOIL AND SUMP MATERIAL SAMPLING
Objectives	Obtain additional soil chemistry data for Remedial Design
Intended Data Use	Risk assessment, compliance monitoring, information to aid in remedial design and characterization for possible disposal options.
Required Analytical Methods of DQO Levels	VOCs (8260) SVOC's (8270) Pesticides (8080) Metals (see Table B.1) Hydrocarbons Petroleum Hydrocarbons (ASTM D-2887) Moisture, Density, Grain Size (ASTM D-2216) Air Permeability (API-RP-40) TCLP Extraction (1311) - Methods (see Table B.1) - VOC's (8260) CamWet (CR66699(A))[1] - Metals
	DQO Level 3[(2)]
Contaminants of Concern	VOCs, SVOCs, Pesticides, PCBs and Metals[(3)]
Required Detection Levels	VOCs[(4)] SVOC's[(4)] Pesticides[(4)] Metals[(4)] Petroleum Hydrocarbons[(4)]
Action Levels/ Regulatory Standards	EPA Interim Action Levels for Benzene and Vinyl Chloride[(4, 5)], Maximum Contaminant Levels (MCLs), EPA/State Hazardous Waste Criteria (e.g., TCLP/STLC) and Site Specific RAOs
Sampling Points	As indicated in Figure A.1
Critical Sampling	Soils nearest to existing buildings

94-256 (Rpts/RdInWo/Rev 2.0-11/17) (11/17/97/ks)

(1) California Waste Extraction test results will be compared to the California Soluble Threshold limit concentrations (STLC).

(2) DQO levels are discussed in Section B.4 of The QAPP (Rev. 2.0), August 1997.

(3) A complete list of contaminants of concern is provided in Table B.1 of the QAPP.

(4) Required detection limits are provided in Table B.1 of the Revised Supplemental QAPP.

(5) EPA interim action levels (EPA, 1997a and EPA, 1997b).

TABLE A.2

APPLICATION OF THE DQO PROCESS FOR SOIL AND SUMP MATERIAL SAMPLING AND ANALYSIS

DQO STEP[(1)]	TREATABILITY STUDY PROGRAM ELEMENTS	
	Chemical Characterization of Subsurface Soils	Geotechnical Evaluation of Subsurface Soils
Statement of the Problem	The objectives of the soil and sump chemical characterization activities are: • Evaluation of COC's in areas not previously evaluated. • Evaluation of COC's in areas where additional data is needed for RD purposes. • Evaluation of COC's in areas near occupied onsite buildings.	The objective of the geotechnical evaluation of the soil and sump materials are: • Evaluation of geotechnical properties (i.e., moisture, density and grain size) for RD purposes. • Evaluation of soil characteristics to determine the applicability of soil vapor extraction (SVE).
Identify Decisions the Data will be used to Resolve	• Determine if sump material presents a site risk. • Determine if sump materials are above RAO's. • Determine if sump material contains leachable constituents above hazardous waste criteria.	The data developed will be used to evaluate the feasibility and effectiveness of SVE in reducing localized areas of subsurface elevated VOCs. In addition, the geotechnical data will be used during the RD process.
State the Variable to be Measured	• VOC's (Method 5035) • SVOC (Method 8270) • Pesticides (Method 8080) • PCB's (Method 8080) • Metals (as shown in Table A.3)	• Moisture (ASTM D-2216) • Density (ASTM D-2216) • Grain Size (ASTM D-2216) • Air Permeability (API-RP-40)
Define Boundaries of the Study Area Including Special and Temporal Units	See Figure A.1.	See Figure A.1.
Decision Rules	• This data will be used to decide if further data needs to be collected to address specific Remedial Design Issues.	• Air permeabilities should exceed 1 Darcy for SVE to be feasible. • Moisture levels should be less than 30% for SVE to be effective. • Density and grain size should be within practical design considerations.
Uncertainty Constraints for the Decision Process	• Non-homogeneity of the site. • Loss of volatile VOC's (i.e., vinyl chloride) during the sampling process.	• Non-homogeneity of the site. • Inherent increases in permeability due to the sampling process.
Optimize the Design within the Constraints of Project Goals	Data will be used in the remedial design process to optimize the design.	Data will be used in the remedial design process to optimize the design.

94-256 (Rpts/RdInWo/Rev 2.0-11/17) (11/17/97/ks)

(1) DQO steps; guidance for the Data Quality Objective Process. EPA QA/G-4 U.S.EPA 1994.

TABLE A.3

LIST OF METHODS AND SAMPLE MATRICES WASTE DISPOSAL, INC.

PARAMETER(1)	EPA METHOD	SOIL SAMPLES	SUMP MATERIALS
Laboratory Parameters			
ICAP Metals (Al, Sb, Ba, Be, Cd, Ca, Cr, Co, Fe, Mg, Mn, Mo, Ni, Na, Th, Va, Zn)	6010	X	X
Arsenic	7060	X	X
Lead	7421	X	X
Mercury	7470	X	X
Selenium	7740	X	X
VOCs	5035	X	X
SVOCs	8270	X	X
Pesticides/PCBs	8080	X	X
Petroleum Hydrocarbons	ASTM-D-2887	X	X
Permeability	API-RP-40	X	X
Moisture/Density/Grain Size	ASTM-D2216	X	X

94-256 (Rpts/RdlnAcWo/Rev.2.0-11/17)(11/17/97/ks)

(1)Table A.2 provides a description of the DQO development process for the constituents of concern. Table A.1 provides a list of the relevant requirements used to establish the detection limits for these compounds.

94-256 TS-06A REV. 11/17/97

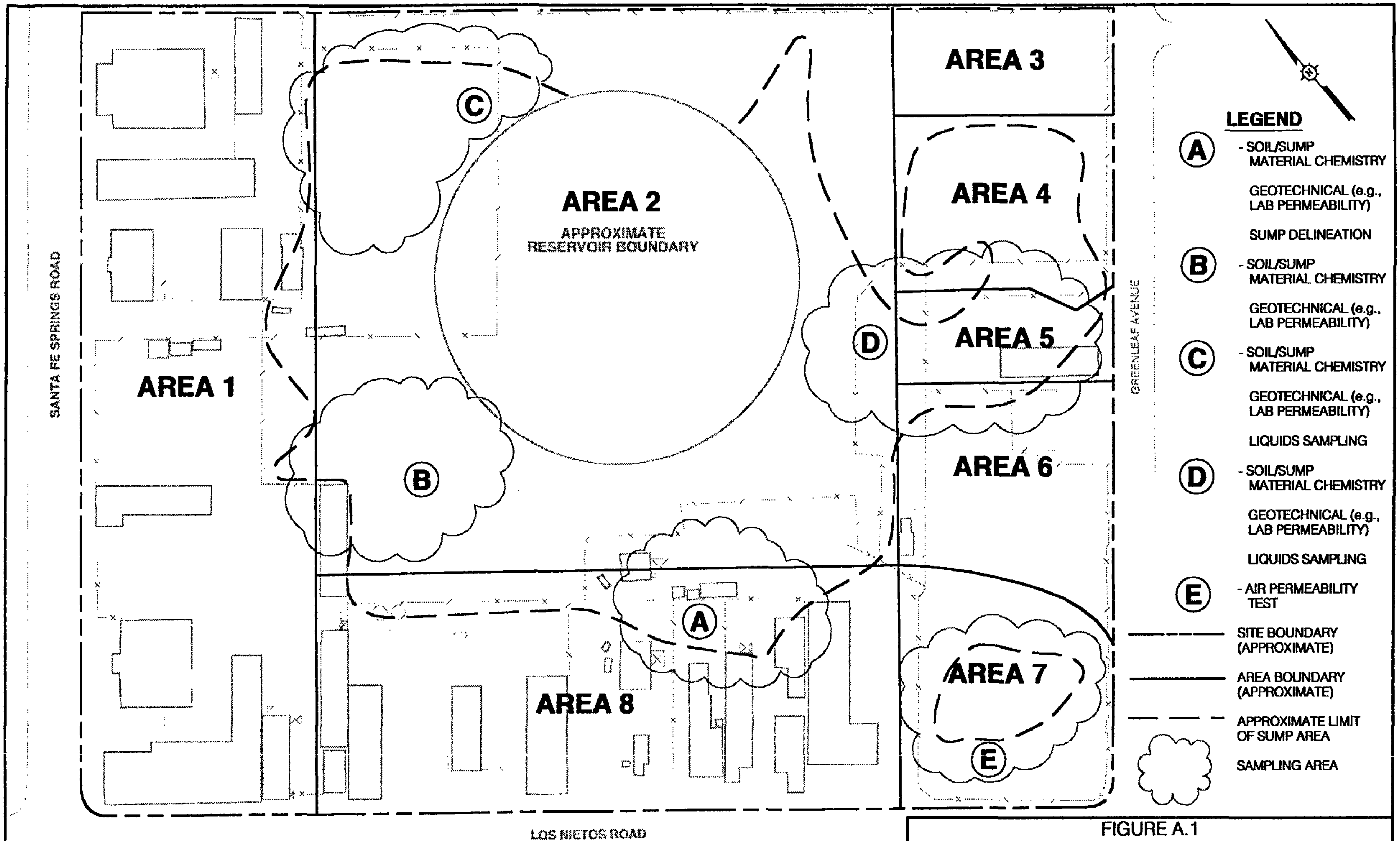


FIGURE A.1

GEOPROBE INVESTIGATION AND SVE CANDIDATE AREAS

WASTE DISPOSAL, INC.
SANTA FE SPRINGS, CALIFORNIA

TRC

REV. 2.0

REFERENCE: BASED ON FIGURES 2.3 AND 2.7, FINAL REMEDIAL INVESTIGATION REPORT, EBASCO, 1989d.

ATTACHMENT A.1

ASTM METHOD D-2887
SIMULATED DISTILLATION OF PETROLEUM HYDROCARBONS

TRC

SIMULATED DISTILLATION

A. Summary

This method is used to determine and characterize FID detectable hydrocarbons C_8 to C_{44} in aqueous, soil, sediment, or product samples by gas chromatography. The characterization of heavier fuels such as diesel, naphtha, jet fuels and crudes may be achieved by this method.

The sample is extracted with pentane and then injected into a gas chromatograph equipped with a megabore column, split injector and flame ionization detector.

B. Safety

1. Analyst should use gloves when handling samples or standards.
2. Safety glasses should be worn.
3. Standards and samples should be prepped in the hood.

C. Apparatus

1. HP 5890 (or equivalent) gas chromatograph equipped with:
   a. Flame Ionization Detector
   b. HP 7673A Autosampler (or equivalent)
   c. Split Injector.
2. Column (Restek 6 meter x 0.53 mm ID sicosteel clad column, 0.1 um thickness or equivalent).
3. Autosampler vials - 2 mL.
4. Graduated pipets - 25 mL disposable.
5. Hamilton syringes - 50 uL, 100 uL, 1000 uL.
6. Repipetor - 10 mL.
7. Top loading balance.
8. Septa must have a maximum operating temperature of 350^{o}C or higher. The septa will need to be changed often -

approximately after every 50-75 injections or 5 days. Supelco Thermogreen LB-2 septa are recommended.

9. Injector liner with glass wool or equivalent. Several should be kept in stock and changed every 3-6 months depending on sample volume. A split liner with half of the glass wool removed is recommended.

D. Reagents

1. Diesel spike solution: 0.100 g neat into 10 mL CS_2 for a 10,000 ppm solution.

2. Carbon disulfide - Aldrich glass distilled HPLC grade or equivalent.

3. 1,3-Dichlorobenzene surrogate: 0.100 g neat into 10 mL CS_2 for 10,000 ppm solution.

4. Calcium chloride, 0.1 M: 1.11 g 4 to 30 mesh or powdered $CaCl_2$ into 1 L water.

6. Calibration standards: individual carbons C_8,C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, and C_{44} should be ordered neat. Prepare a working standard of 4000 ppm of C_8-C_{40} and 800 ppm pf C_{44} standard by weighing out 0.1g of C_8-C_{40} and 0.025g of C_{44} into a 25 ml volumetric flask. Dilute to mark with CS_2. Calibration levels should be 50, 100, 200 and 300 ppm for C_8 to C_{40} and 12.5, 25 and 75 ppm for C_{44}.

5. Calibration check standard, 100 ppm: From the 4000 ppm solution, prepare a 100 ppm C_8-C_{40} and 25 ppm C_{44} in CS_2 by placing 25 uL of the 4000 ppm solution in 1 mL CS_2.

E. Procedure

1. Notebook Preparation

a. Enter the date, the instrument number and the analyst's initials in the header.

b. Prepare columns for log number, sample description, client name, sample weight, final volume and comments.

c. Prepare the runlog by entering the date and analyst's initials in the header. Enter the log number of each sample to be run, the dilution (if any) and the data file name (the chromatogram number) in the appropriate columns of the run log.

2. Soil Preparation

a. Tare a 40 mL vial in the toploading balance.

b. Open the core and discard the top 2 inches of soil.

c. Weigh 10 g of soil into the vial.

d. Record the sample weight in the prep book.

e. For matrix spikes, weigh out additional portions of sample and add 100 uL of a 10,000 ppm diesel solution. This will give a concentration of 1000 ppm.

f. For LCS, transfer 10 mL of CS_2 to an empty vial and add 1 mL of 10,000 ppm diesel.

g. For a method blank, transfer 10 mL of CS_2 to an empty vial.

h. Add 100 uL of surrogate to all samples including blank, spikes and LCS.

i. Add 2 mL of $CaCl_2$ to all soil samples, spikes and blank.

j. Add 10 mL of CS_2 to all samples and spikes.

k. Shake vigorously for two minutes.

3. Aqueous Sample Preparation

a. Pipet 25 mL of sample into a 40 mL vial. Sample should be taken from vials with no headspace.

b. For matrix spikes, pipet additional portions of sample into 40 mL vials. Add 100 uL of the 10,000 ppm diesel.

c. For the LCS, add 10 mL CS_2 to an empty vial. Add 100 uL of 10,000 ppm diesel solution.

d. For a method blank, transfer 10 mL of CS_2 to an empty vial.

e. Add 100 uL of surrogate to all spikes, blank, LCS, and samples.

f. Add 10 mL of CS_2 to all samples and spikes.

g. Shake vigorously for two minutes.

4. Sample Analysis

a. A CS_2 blank should be run to check for instrument contamination.

b. Initially calibrate the instrument by injecting 3 calibration standards (section D.6) for the individual carbons. The diesel standards should be run at 500, 1000 and 3000 ppm. The correlation coefficient should be at least 0.980.

c. Run the calibration check standard of C_8 to C_{40} and C C_{44} at 25 ppm mix at 100 ppm.

d. If the calibration check meets the criteria in section F, load the autosampler with method blank, samples, spike, duplicate spike, and LCS.

e. A pentane wash should be run after any sample where the pentane has turned dark or yellow to help prevent contamination from carryover.

5. Instrument Conditions

a. Oven temperature
   Initial - 40°C
   Initial Hold - 5 minutes
   Rate - 20°C/minute
   Intermediate Temperature - 320°C
   Intermediate Hold - 6 minutes
   Final Temperature - 380°C
   Final Hold - 0 minutes
Detector Temperature - 330°C
Injector Temperature - 320°C

6. Autosampler Conditions

Injection time - 0.02 minutes
Injection volume - 1 uL
Split flow - 30 mL/minute
He:8 mL/minute
He:30 mL/minute
Air:350 mL/minute
N_2:30 mL/minute

F. Quality Control

1. The calibration curve should have a correlation coefficient of at least 0.980.

2. The concentration of the calibration check must be within 25% of the expected value. If not, rerun the calibration check.

3. A matrix spike, matrix spike duplicate and LCS must be run every batch.

4. The LCS recovery should fall between the in-house determined control limits.

5. The percent recovery of the matrix spike should fall within in-house determined control limits. If not, check the LCS. If the LCS is within the control limits, the results can be reported.

6. A reagent (method) blank must be run with each batch.

G. Calculations and Data Review

Individual carbons:

Example: C_8-Add up the area between the retention times for C_8 to C_{10}. Include areas exactly on C_8 and up to but not including C_{10}.

Take this area and multiply by the response factor. This will equal your ppm amount for C_8. Follow this procedure for carbons C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, and C_{44}.

Total fuels:

When requested by a client simulated distillation can be calculated against a regular fuel calibration.

Example:

Total area (minus surrogate) times response factor. The response factor can be from a diesel, oil, or other fuel calibration.

$$\text{Response Factor} = \frac{\text{Concentration of Standard}}{\text{Area Count of Standard}}$$

$$\text{Concentration of Aqueous (mg/L)} = \frac{As \times RF \times Ve}{Vs}$$

$$\text{Concentration Soil (mg/Kg)} = \frac{As \times RF \times Ve}{Ws}$$

where:

As = Area count of the sample
RF = Response factor
Ve = Volume of the methylene chloride extract
Vs = Volume of the aqueous sample
Ws = Weight of the soil sample

Carbon range:

Carbon range is determined by comparing with the retention time of Carbons C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, C_{44}.

Characterization:

Characterization is done by matching the pattern with various types of fuels such as diesel, jet fuel, and motor oil.

H. Interferences

1. Any non-fuel compound which responds to FID detector will interfere with fuel analysis.

I. Troubleshooting

1. Low spike recovery.

   Check the surrogate recovery. If the surrogate recovery is also low, check for leaks and re-run the sample.

2. Excessive cross-contamination.

   a. Bake column at 350°C for at least one hour and then run several pentane washes.

   b. Replace the glass insert and cut the column at the injector end.

M. References

1. SOP Jones Environmental

2. ASTM Method 2887

Reviewed and approved
L. Geddes 03/11/96
Issued OKG 3/11/96

ATTACHMENT A.2

ASTM RECOMMENDED PRACTICE -40 (RP-40)
AIR PERMEABILITY TESTING

API
RECOMMENDED PRACTICE
for
CORE-ANALYSIS PROCEDURE

OFFICIAL PUBLICATION

REG. U.S. PATENT OFFICE

AMERICAN PETROLEUM INSTITUTE
Washington, D. C.

Issued by
AMERICAN PETROLEUM INSTITUTE
Production Department
211 N. Ervay, Suite 1700
Dallas TX 75201

Users of this publication should become completely familiar with its scope and content. This document is intended to supplement rather than replace individual engineering judgment.

TABLE OF CONTENTS

RECOMMENDED PRACTICE
for
CORE-ANALYSIS PROCEDURE

Foreword

a. This recommended practice was formulated by the Subcommittee on Core-analysis Procedure, the membership of which is listed below. It is published under the sponsorship of the Steering Committee on Production Practice and the Executive Committee on Drilling and Production Practice, of the Institute's Division of Production.

b. This recommended practice has been prepared with two uses in mind:

1. As an aid in selecting methods of core analysis applicable to a specific problem. A comparison of various reliable methods is made under each core-analysis practice, giving a brief statement of the principles, advantages, and limitations.
2. As a guide in testing. Representative procedures for the various core-analysis methods are described in some detail for those wishing to use the recommended practice for this purpose.

c. The content of this recommended practice was gathered by a representative of each API district from operators and service companies actively using core analysis in that district. These data were compared and screened to meet the needs of many types of samples. Only techniques which are known to give reproducible and accurate results on a routine basis have been included in the final composite. Acknowledgment is made to these companies for their contributions to this effort.

SUBCOMMITTEE ON CORE-ANALYSIS PROCEDURE

Gerould H. Smith, *Chairman*, Union Oil Co. of California
G. T. N. Roberts, *Vice-Chairman*, Shell Oil Co.
John De Petro, Consultant
E. H. Koepf, Core Laboratories, Inc.
T. A. Johnson, Southern California Gas Co.
Henry Lewelling, The Atlantic Refining Co.
Larry Powell, The Ohio Oil Co.
R. V. Randall, Humble Oil & Refining Co.
P. O. Wroten, Mobil Oil Co.

1.0 GENERAL FOREWORD

The objective of this manual is to present recommended acceptable practices for routine core analysis. These selected methods are based on sound scientific principles and will yield data that are reproducible and significant to the resolution of the problems for which the data are intended. Routine core analyses, for purposes of this recommended practice, have been defined as determination of fluid saturations, porosity, and gas permeability. Core-water salinity and oil gravity have been added as supplementary tests.

Core analysis provides direct measurement of some of the basic rock properties which are needed to determine the total fluid content, the distribution, and the flow behavior of the reservoir fluids or injected fluids. The importance of reliable and representative core data cannot be over-emphasized. These data are basic in evaluating oil reservoirs. The interpretation of other logging methods is established by correlation with core-analysis data.

Core-analysis problems fall into two general categories, viz., the determination of basic data and the interpretation of the analytical results. The determination of reliable basic data depends upon the intelligent selection of test samples, the careful preparation of these samples for testing, and the use of test methods and equipment based on proved scientific principles. The proper interpretation of the analytical results must be based on understanding of the changes which occur during coring and lifting the core to the surface.

All currently used coring procedures alter in some degree the fluid content of the reservoir rock during the coring process. The drilling fluid is jetted against the formation ahead of the coring bit and against the peripheral surface of the core as it passes into the core barrel. The core is thus subjected to the flushing action of the drilling-fluid filtrate. Some of the factors which contribute to the degree of flushing are: *1*, rate of bit penetration; *2*, vertical and horizontal permeability of the formation; *3*, filtrate-loss properties of the drilling fluid; *4*, pressure difference between the drilling-fluid stream and formation; and *5*, core diameter. Since the bit and core barrel tend to remove filter cake from the surface of the core, the degree of flushing varies more with drilling-fluid pressure and rate of coring than with fluid-loss properties of the drilling fluid. Normally, most free gas and a portion of the liquid content are displaced from the core by drilling-fluid filtrate. In many cases, where water-base drilling fluid is used, the flushing action of the drilling-fluid filtrate may displace the oil until, at complete flushing, the oil saturation is decreased to what is considered the residual-oil saturation of the sample. The original water contained in the rock may also be displaced by the flushing action to such an extent that the fluid content of the recovered core may be predominantly from the drilling fluid.

As the partially or completely flushed core is brought to the surface, the pressure and temperature are reduced from reservoir to atmospheric conditions. The gas dissolved in the oil and water expands and subjects the core to a solution-gas drive and expulsion of liquids continues as the core nears the surface and the pressure declines. Thus, the core as recovered at the surface may have been subjected to the equivalent of a liquid displacement, followed by a solution-gas drive. Recognition that these conditions are imposed on the core is essential to proper interpretation of the data from core analysis.

Differences in rock characteristics, the type of core sample recovered, or additional tests to be made on the sample often require that a specific procedure be used for testing a given core. Thus, this recommended practice lists a number of different procedures for some of the various core-analysis measurements. The major principles involved, the types of data obtained, the procedures, and the advantages and the limitations of the various recommended core-analysis procedures are presented.

2.0 FIELD CORE SAMPLING AND PRESERVATION

Field sampling of cores should represent the best possible practices because the value of all core analysis is limited by this initial operation. The objective of a standard field core-sampling procedure is twofold:

a. To obtain samples which will give results representative of the formation.

b. To obtain samples under a uniform procedure so that the results will be independent of the sampler.

The two major problems confronting those sampling reservoir rocks for core analysis are:

a. The selection of representative samples from each core.

b. The wrapping and preserving of the core samples quickly enough to prevent loss of fluids from within the core or the absorption of foreign fluids by the core.

The selection of samples is fairly simple for relatively uniform formations. However, where a formation contains widely varying lithology and heterogeneous porosity types — such as conglomerates, weathered cherts, vugular or fractured carbonates, and inter-laminated shales and sands — the proper selection of representative samples requires greater care. A trained person — engineer, geologist, etc. — should follow a fixed sampling procedure at the well location. All or portions of the core should be preserved and sent to the laboratory according to kind of rock cored, amount of recovery, and purpose of laboratory analysis. The actual preservation of the core fluids and the distribution of the fluids in the core as sampled are the most important objectives of core preservation. In order to obtain these, a uniform procedure for sampling and preservation must be conducted. The following procedures have been selected as those which will yield samples that allow the most reliable and representative core analysis.

2.1 CORES FOR CONVENTIONAL CORE ANALYSIS

2.11 SAMPLING

2.111 Removal from the Core Barrel

Cores should not be allowed to remain in the core barrel after reaching the surface since fluids from the mud may be absorbed by capillarity. This will change the equilibrium conditions established by expanding gas as a sample comes to the surface. Any delay in removal of the core from the barrel should be noted and reported.

The core should be removed from the core barrel as gently as possible to cause a minimum alteration of the core and its fluid content. It is recommended that the core either be allowed to slide gradually from the barrel by gravity, by raising one end of the barrel, or by pushing it using a plunger or rod. Light hammering or jarring may be necessary to move the core, particularly hard cores. However, heavy hammering or pounding the core barrel on its end should be avoided. These rough practices may alter the core, especially if it is a soft sand. Even in a more consolidated core, jarring and hammering may cause part of the core to become crushed or fractured.

Only if the core cannot be removed by the foregoing methods should it be pumped out with a fluid. If this is necessary, a suitable piston arrangement should be used which will not allow fluids to contact and to contaminate the core. The drilling fluid should be used if pumping directly with fluids is necessary. The use of fresh water or other fluids foreign to the core should be avoided. If water is forced past the piston and forced into a core, high water-saturation values will be obtained by core analysis. Any excessive pressuring of the barrel may cause some fluid from mud and mud cake to penetrate the core. Any difficulty or irregularity in removing the core should be noted, e.g., pressure used if pumped out with mud, loss of consolidated material, etc.

2.112 Labeling and Logging of the Core

The cores as they are removed from the core barrel should be placed in appropriately marked trays or troughs taking care to keep the tray sequence and orientation in order. Protection from high temperatures, i.e., direct sunlight, hot engines, etc., or from rain, strong wind, etc. should be provided. Accurate measurements of recovery should be made and recorded. Any recovery in excess of the core cut should be reported, as well as any lost recovery. Log the lost recovery at the bottom of each core interval, unless some special observation indicates an exception should be made. Such exceptions should be noted. The engineer or person in charge should use the best information available when allocation of lost recovery is required. Data and observations such as the following are always helpful.

a. Drilling time per foot (may indicate formation breaks).
b. General conditions of the core (continuity, broken section, etc. should be noted).
c. Condition of the core catcher (if badly damaged, bottom of core may have dropped out and may be subsequently recovered).

In some cases, it may be possible to assign lost recovery to a more exact depth by using electrical or other types of surveys.

2.113 Cleaning the Core

It is recommended that the core be wiped to remove soft mud cake and excess mud as soon as possible following its removal from the core barrel. The excess mud should be wiped off with a damp—not wet nor dry—rag. Preferably, the rag should be dampened in drilling fluid and wrung out as often as necessary to prevent its becoming too wet. Core samples to be sent to the laboratory should never be washed with water or any other liquid after removal from the barrel. Depending upon the firmness of the core, there may be a question whether the mud cake should be removed either by wiping with a rag or scraping with a knife. If field examination is required, it may be necessary to scrape part of the core in order to make the examination. Emphasis must be placed on never washing the mud from the core. In any event, the wiping, examination, and sampling procedure following removal from the core barrel should take a minimum of time. The time a core is exposed to the drilling fluid and the atmosphere will affect the subsequent core analysis.

Even a few minutes exposure of cores, depending upon atmospheric conditions, can cause the loss of both water and light hydrocarbon fractions. Tests have shown that as little as ½-hour exposure to the atmosphere can result in 10- to 25-percent loss in water content. If the core is accidentally washed with water, allowed to remain in the core barrel, or let stand before sealing in a container, then a notation of the washing, the number of hours in the core barrel, or the length of exposure time before sealing in the container should be made.

2.114 Frequency and Size of Sample

Retaining the entire core is the preferred practice. Where the entire core is not retained, it is recommended that at least every foot normally be sampled. Some consideration should be given to the proper statistics of sampling for various types of rocks.[1, 2, 3]

Where cores are not entirely saved, it is desirable that those samples selected should be a minimum of 4 in. to 6 in. in length. *All cores taken by wire line should be saved.*

2.115 Sampling Procedure Where the Entire Core Is Not Saved

The following sampling procedure is recommended to minimize the time a core is exposed to both drilling fluid and the atmosphere.

a. As soon at the recovery has been accurately measured, sufficient mud cake is removed to allow inspection and a proper selection of samples. The core should be cleaned of excessive mud by wiping, wrapped with foil or plastic to minimize changes in the core, and replaced in the proper position in the tray.
b. The lithology and the depth of the samples should be accurately determined and recorded.
c. The samples should then be packaged in a manner consistent with the test desired and the expected time lapse before testing.
d. Both the samples and the container should be labeled with the well name and depth. Any additional pertinent data should accompany the cores to the testing laboratory.
e. If exposure is longer than 30 min., conditions of weather, temperature, etc. should be noted. Any large time lapse between sampling the first section of a given core and the last section should be noted.

[1]References are given in Section 8.0.

2.116 Data Sheet

A suitable data sheet should be provided for and completed by the sampler to supply as complete a record as possible of the conditions of sampling. This record will be valuable in qualifying interpretation of the subsequent core-analysis data. Further, this record may suggest either that certain additional tests be run to supplement routine tests, or that certain tests would not yield significant data. This will result in the most useful data for the least time and money. Fig. 2.116F1 is an example form, and the use of this or a similar form is recommended.

It is important to have as much pertinent data as possible accompany the sample. Following is listed the desirable information:

a. A description of the lithology.
b. A designation of the mud type, weight, filter loss, chlorides, and chemical treatments.
c. Gravity of the oil produced in that zone.
d. Designation of tests desired.
e. Person's name to whom data should be reported via telephone, air mail, or regular mail.
f. Company, field, well, and zone.
g. Any pertinent data not listed, e.g., time core exposed before sampling, weather, diffculty in removing from core barrel, time to pull core, etc.
h. Core record and drilling log.
i. Well logs (if available).
j. Well elevation, designated as kelly bushing (KB) or ground level (GL).

2.12 PRESERVATION OF CORES FOR ANALYSIS

The preservation of a core is an attempt to maintain it, prior to analysis, in the same condition as existed upon its removal from the core barrel. In the process of cutting a core, recovering it, and bringing it to the surface, the fluid content of the rock is altered by unavoidable processes. Careless or incorrect practices in sampling and packaging cause further alteration of the core and its fluids, thereby making the core even less representative of the formation conditions.

Preservation and packaging of cores may vary depending upon the test required and the length of time before testing. If the core samples selected for analysis are to be analyzed for fluid content, it is necessary that they be preserved for transportation to the laboratory in such a way as to prevent the evaporation of liquids and the migration of fluids within the sample itself.

An additional objective of the preservation is to prevent breakage of the cores during shipment and storage. Hard and consolidated cores may be durable enough not to require special precautions for support. However, special care should be taken to give adequate support to cores which are soft or poorly consolidated. The use of a container of approximately the same diameter as the core may prevent breaking of some loosely consolidated samples during shipment. Aluminum foil may be used to protect loosely consolidated sand from damage during shipment.

The use of glass jars, easily deformable plastics, paper cartons, and other non-rigid containers should be avoided if the core samples are to be shipped or will be subjected to other rough handling. Metal or rigid plastic containers are recommended.

2.13 METHODS OF PRESERVING CORES UNTIL TESTED

The best preservation method will be the one that experience indicates to be most satisfactory for the type of core in question. Frequently, the method will depend upon the nature of the rock. Therefore, general use of one specific method of preservation may not be proper. Further, the techniques required to preserve cores for testing may depend upon the length of time for storage and the nature of the test desired. Some variation in the technique of preserving the cores may depend upon whether the cores will be tested in local areas or whether they must be prepared for long-distance shipping. Preferred methods to preserve cores for laboratory analysis, without significance to the order of listing, are:

a. Sealing in air-tight metal cans.
b. Sealing in steel, aluminum, or plastic tubes, using suitable couplings, pipe caps, or O-ring seals.
c. Sealing in plastic bags.
d. Freezing with dry ice.
e. Wrapping in metal foil or plastic tape.
f. Coating with plastic.

2.131 Sealing in Air-tight Cans

Core samples selected for analysis, particularly when saturation determinations are critical, may be sealed in metal cans. This is an efficient, rapid method. Cores may be canned directly or sealed in cans after a preliminary wrapping using aluminum foil, or polyethylene or other suitable plastic. There should be a minimum of space between the core sample and the can, particularly if no preliminary wrap is used. If the core is friable, some provision to prevent its movement in the can during shipping should be made. The use of paper, wax paper, cardboard, or materials which may absorb moisture or oil from the core should be avoided. If the entire core is shipped to the laboratory following the selection and canning of samples for fluid-saturation tests, the canned samples — each properly labeled for depth — may be replaced in the position from which they were removed from the core. The core should be properly logged on its arrival at the laboratory. Normally, it is recommended that cores not be canned with any fluid surrounding the core. The sealed container should not be subjected to large temperature fluctuations, if possible, in order to minimize evaporation and condensation of core fluids in the container.

2.132 Sealing in Air-tight Steel, Aluminum, or Plastic Tubes

Using suitable couplings, caps, or O-ring seals, the entire core may be preserved for analysis by placing it in steel, aluminum, or plastic tubes. A close-fitting tube is desirable. Normally, no fluids should be used in packaging the cores although the cores may be pre-wrapped in plastic or metal foil. Large variations in temperature during storage and shipment should be avoided.

2.133 Sealing in Plastic Bags

Core samples which are sealed in plastic bags should have a minimum of air space between the core and the bag wall. Any excess bag can be folded against the core wall and taped in place to assure a tight fit. Excess air may be withdrawn by suction. Care must be taken in adjusting the bag so that sharp points on the core do not puncture the bag. In some cases, more than one layer of plastic bag or sheeting may be used for wrapping cores. Cores sealed in plastic bags may be packed in boxes with suitable packing to prevent their being broken in shipment, or they may be canned or placed in metal or plastic tubes. The same precautions must be observed for cores sealed in plastic bags as for those sealed in cans, so far as exposure to extremes of temperature is concerned.

DATA FOR CORE ANALYSIS

1. Operator ____________
2. Well ____________
3. Field ____________
4. County ____________
5. State ____________
6. Location ____________
7. Elevation ____________ {GR / DF / RB}
8. Formation ____________
9. Core recorder? Yes ______ No ______
10. Crude-oil gravity ______ ° API Est. ______ Meas. ______
11. Formation-water chlorides ______ ppm
12. Analysis requested:
    a. Routine core analysis
    - ☐ Fluid saturation
    - ☐ Porosity
    - ☐ Permeability
    - ☐ ____________
    - ☐ ____________

    b. Special tests
    - ☐ ____________
    - ☐ ____________
    - ☐ ____________
    - ☐ ____________
13. Core No. ______
14. Date cored ______
15. Sampled by ______
16. Date shipped ______
17. Shipped by ______
18. Shipped via ______
19. Type of core:
    - ☐ Conventional
    - ☐ Diamond
    - ☐ Wire-line
    - ☐ Side wall
    - ☐ Cable-tool
    - ☐ ____________
20. Drilling-fluid data:
    - Type ______
    - Weight ______
    - Viscosity ______ Marsh sec.
    - Water loss ______ cc/ ______
    - Chlorides ______ ppm
    - pH ______
21. Send preliminary results
    - To ____________
    - At ____________ Results Desired
    - By ____________ (Hour—Day)
    - For ____________ (Operation)
22. Analysis requested by ____________
23. Lithologic abbreviations:[4]

anhy—anhydrite	gyp—gypsum	sa—rock salt
cht—chert	ig—igneous	sd—sand
cly—clay	ls—limestone	sh—shale
cgl—conglomerate	meta—metamorphic	slt—silt
dol—dolomite	mrl—marl	ss—sandstone

24. Remarks ____________

DEPTH | SYMBOL | DESCRIPTION

SCALE: ½″ = 1′

FIG. 2.116F1—EXAMPLE FORM FOR CORE-ANALYSIS DATA

2.134 Freezing with Dry Ice
(U. S. Patent No. 2,617,296)

Cores which are preserved by freezing should be frozen very rapidly by application of dry ice. Slow freezing may result in the migration of fluids within the core structure or breakage of the core. Cores are commonly frozen when the core-analysis laboratories are local. Preservation by freezing of cores for extended storage requires refrigeration or continuous repacking with dry ice. If it is necessary to allow the core to warm to room temperature before testing, the condensation of moisture from the atmosphere onto the core surface must be prevented. Slow thawing of the core will cause some redistribution of the fluids within the core matrix.

Freezing will affect properties of cores flushed with fresh water more than those flushed with saline mud filtrate. These effects will decrease with liquid saturation.

2.135 Wrapping in Metal Foil and Plastic Tape

Cores should be wrapped with metal foil and plastic tape only if they are consolidated enough to withstand shipment and will be analyzed in a few hours. Care must be taken that the foil is not punctured by sharp points of the core. To preclude this, cores are often double- or triple-wrapped. Effective wrapping with metal foil is best accomplished by lapping the edges along the length of the core as well as on the ends and folding once or twice, finally pressing the folded edges down against the core. The use of a self-sealing vinyl tape has been substituted for plastic, after foil wrapping. Foil wrapping prevents the adhesive on the tape from absorbing oil from the core.

2.136 Plastic Coatings

Plastic coatings have been used where cores are not to be tested within a few hours and need to be transported over distances which may involve rough handling. The cores should be scraped reasonably free of mud cake, dipped in the molten plastic, tagged, and shipped in this condition. One procedure used for dipping cores in molten plastic requires a thermostatically controlled melting pot to hold the plastic in a barely melted condition. The core to be coated is grasped by tongs or by the thumb and forefinger at one end, submerged about two-thirds of its length in the molten plastic, immediately removed, and allowed to cool and set for a few seconds. It is then grasped by the coated end and dipped, allowing the second plastic layer to overlap the initial one.

A dip such as that just described should leave a plastic layer about $\frac{1}{16}$-in. thick, completely surrounding and sealing the core with no air space between, yet not penetrating the core beyond one sand grain depth. If transportation over long distances is anticipated or if cementation of the core is not good, it may be advisable to repeat the dipping process, thereby building up the thickness of the coating. This can be continued to achieve any reasonable thickness desired. However, for normal physical protection, the initial dip coat is satisfactory. Very poorly consolidated cores may be wrapped in foil before dipping.

Plastic used for coating cores must have certain properties, as follows:

a. It must be dimensionally stable over long periods of time.
b. It must not react with oil or water.
c. It must not contain oleic acid, oil, solvent, or any other liquid which may be exuded when set.
d. It must be impermeable to gases, oils, and water when set.
e. It must have a low melting point, preferably below 200 F. maximum.
f. It must have a fairly low viscosity when melted. The viscosity should be similar to that of an average oil paint such that it will pour readily or drip slowly from a small opening, yet will not quickly penetrate capillary openings.
g. When removed from heat and exposed to normal air temperatures, it should dry and set tack-free within 5 to 15 sec.
h. When set, it should be tough but pliable, slightly elastic but with good tensile strength, and not melt at temperatures below 180 F.

2.14 PRECAUTIONS

Sampling and wrapping should be conducted in such a manner as to prevent both loss of the interstitial fluids and contamination with foreign fluids. Thus the core should never be washed with water or oils before packaging. For a reliable determination of fluid content of cores, a uniform procedure must be observed for core sampling and preservation. Some precautions for packaging samples are listed.

a. All samples should be sealed in containers as soon as possible after removal from the core barrel. Even after sealing, the samples should be kept at reasonably constant temperature to prevent evaporation and condensation in the packages.
b. Use a can or container with approximately the same diameter as the core to minimize the air space between the core and the sample which might lead to evaporation losses. This will also minimize condensation losses on the inside surface of the container and prevent breaking of the more loosely consolidated samples during shipment.
c. Do not put cloth, paper, cellophane, wax paper, or any material with fine capillaries in the container if a fluid-saturation test is required, unless the core is adequately protected by methods described.
d. Do not dip the core in wax.
e. Unconsolidated sand cores require very careful handling. Place in a container only material that is least contaminated with drilling mud. In such cases, it is more useful to have a small, clean sample than a large, badly contaminated one. When the sand and drilling mud are mixed together, there is little use in canning the sample. However, if a test is desired to determine the presence of oil, as clean a sample as possible should be canned and a notation made on the label that the sample is contaminated with drilling mud. Thus unnecessary laboratory testing and improper interpretation of the tests which are made can be avoided.
f. Do not can an unconsolidated sand sample in the same container with a consolidated or hard sample.
g. Should any core be accidentally washed with water or oil, a notation of the washing or exposure should be made.
h. Label each container properly, indicating well name and depths of interval represented.

i. If the engineer or person in charge is not able to be on location when the core is pulled, he should leave instructions for the core to be preserved in containers according to the foregoing rules. Inspection and description of the core could be made later at the well site or, preferably, at the laboratory when opening the container for analysis.

j. Cores which are canned should have the interior of the can inspected for free oil and water at the time of opening.

k. Upon arrival at the laboratory, cores should remain sealed in their original containers until time for analysis.

2.2 CORES FOR FULL-DIAMETER CORE ANALYSIS

In several principal producing formations, the major porosity and permeability are due to fractures and solution cavities. The samples used in conventional core analysis are too small to properly evaluate these non-homogeneous formations. Procedures have been developed to use full-diameter cores for analysis and thus obtain the maximum sample size.

2.21 SAMPLING

2.211 Sampling and Cleaning the Core

Identical sampling procedures and precautions used for conventional core analysis should be used in the sampling and well-site cleaning of cores on which full-diameter core analysis is to be obtained (see 2.11). Breaking the core into small sections for visual examination should be held to a minimum. Sample sections of 12 to 20 in. should be marked off along the entire core in order to take advantage of the long pieces recovered. Some samples may consist of a single 12- to 20-in. piece; whereas other samples may be composed of several pieces, 4 in. or longer.

2.212 Frequency of Sampling

Retaining the entire core is the preferred practice. If the entire core is not retained, it is recommended that at least every foot normally be sampled. Those samples selected should be a minimum of 4 in. to 6 in. in length. Some consideration should be given to proper statistics of sampling.[1,2,3]

When the core is received at the laboratory, it should be examined closely. Detailed information is frequently desired relating to the number, size, and major linear direction of fractures, size and distribution of vugs, and abrupt changes in lithology.*

2.213 Data Sheet

Refer to 2.116.

2.22 PRESERVATION OF CORES FOR ANALYSIS

The objectives and methods used for preservation of full-diameter cores are the same as for conventional core analysis. Refer to 2.13.

2.23 PRECAUTIONS

Refer to 2.14.

---

*Some laboratories are equipped to photograph a 50-ft section of core, and enlargements can be made of sections of particular interest for detailed study of the fracture or vug system. Other test equipment for use at this stage of analysis, now available in some laboratories, involves a gamma-ray unit for obtaining a log of the core on the layout table. A comparison of this detailed gamma-ray log and the corresponding analysis and visual examination of the core with a "down-hole" log permits precise and accurate selection of the completion depths in zones of alternating pay and non-pay intervals.

2.3 UNCONSOLIDATED AND SIDEWALL SAMPLING AND PRESERVATION

Unconsolidated samples, sidewall samples, and other small samples normally will not yield reliable quantitative data. If such samples can be tested by conventional analysis, then procedures in that section should be followed. However, in most cases, one can expect only qualitative results. They will be chiefly useful for lithology, tests for the presence of oil, and well-log correlation.

2.31 UNCONSOLIDATED SAMPLES

Unconsolidated samples should be sampled to give a small, clean sample, rather than a large, contaminated one. Because of the fragile condition of many unconsolidated samples, they should be handled with as much care as possible. Place in the container only material that is uncontaminated with drilling fluid. If the drilling fluid and sand are mixed together, there is little use in canning the sample. However, if it is desired to test for the presence and properties of oil, as clean a sample as possible should be preserved and a notation made on the label that the sample is contaminated with drilling fluid. Such a notation will prevent unnecessary laboratory testing and improper interpretation of the tests which are made.

Metal foil may be used to support and protect loosely consolidated samples. The metal foil may be folded carefully around the sample and shaped to conform to the sample.

2.32 SIDEWALL SAMPLES

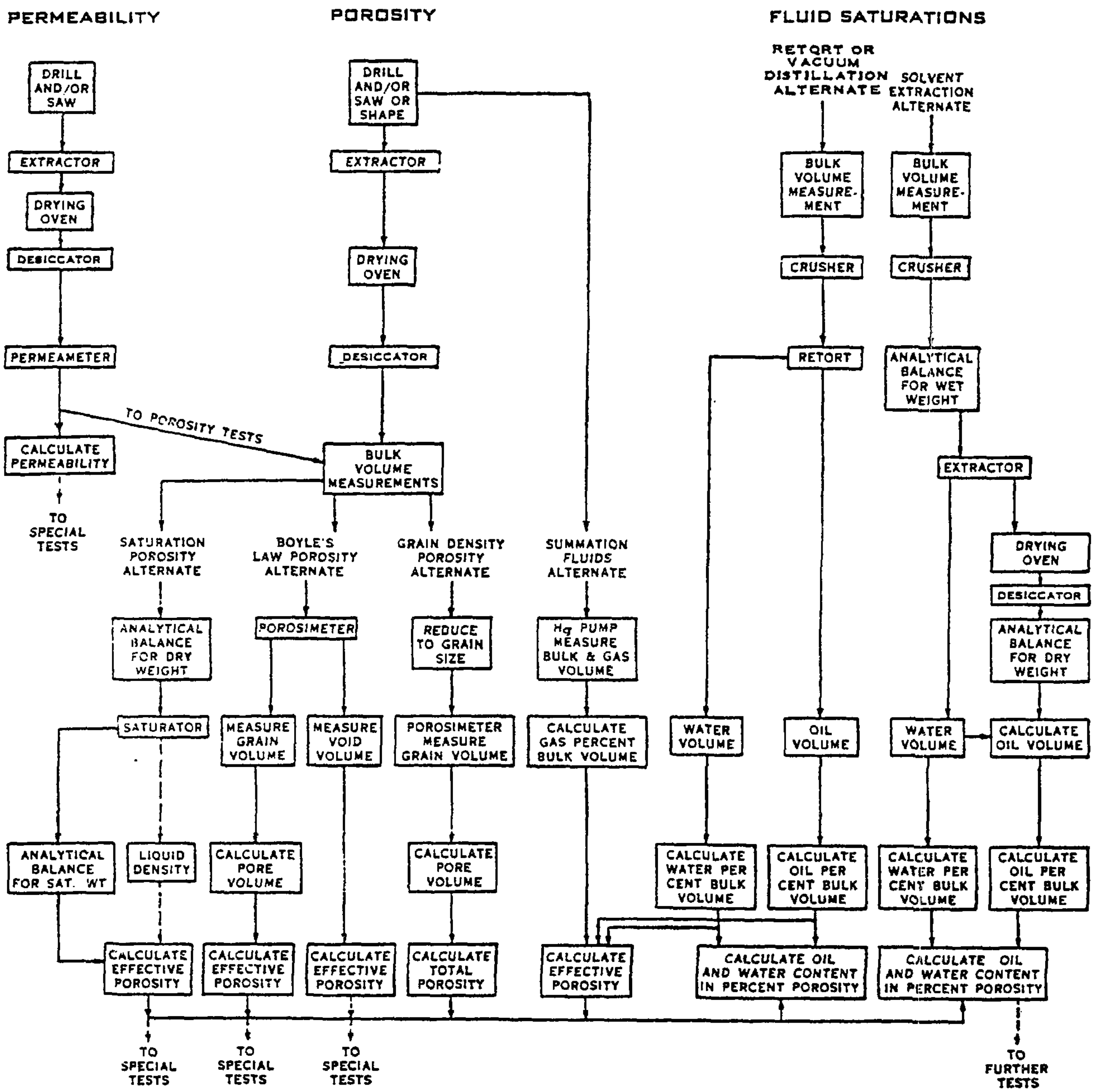
Sidewall cores should be carefully removed from the coring instrument. They should not be broken or squeezed if any core analysis is intended. Sidewall coring barrels should not be washed after being pulled out of the hole until after the cores have been removed. Sidewall samples to be used for core analysis must be delivered to the laboratory in the same state, as nearly as possible, as when removed from the barrel.

Tests show that sidewall samples taken by percussion exhibit changed permeability and porosity as well as grain fracture. Punch samples do not seem to show as much distortion, but sometimes have altered fluid content resulting from mud contamination. Rotary-cut sidewall samples are best for core-analysis testing.

The samples taken from the core barrel should be placed immediately in glass jars or other non-absorbent containers. These jars should be tightly closed and sealed, e.g., by a piece of tape wrapped around the glass-to-metal contact to insure that the core container is air-tight. Such containers should be shipped to the laboratory in suitable boxes to prevent core or glass breakage from rough handling. The samples should remain in the sealed jars until testing is carried out.

3.0 CONVENTIONAL CORE ANALYSIS

CONVENTIONAL CORE-ANALYSIS PROCEDURES



(A schematic flow sheet of the routine core analyses described in Section 3.1.)

3.1 LABORATORY CORE PREPARATION

The preparation of core samples for laboratory analytical procedures must, of necessity, be dependent upon:

a. The data desired on the particular core to be analyzed.

b. The type of rock or formation from which the core was taken.

c. The coring technique involved in cutting and bringing the core to the surface.

For example, if fluid saturation data are required, the core must be carefully and expeditiously handled in the laboratory so that the fluids in the sample remain relatively undisturbed until the analysis has been undertaken. Many formations contain clays which are susceptible to swelling or chemical reaction when contacted with fresh water, thereby altering the basic characteristics (porosity and permeability) of the rock. Therefore, any fluids which contact the samples during cutting and handling of the sample prior to analysis must not in any way damage the sample or displace any of the native fluids in the sample. Prolonged exposure to sunlight, air, or heat will greatly affect the fluid saturations in the sample prior to analysis. It is, therefore, important that the samples be analyzed as soon as the preservation medium has been removed.

3.11 CUTTING OF SAMPLES

The core containers should be opened one at a time and each 1-ft section of core (or as requested) divided into representative portions for the determination of porosity, permeability, and fluid saturation. The portion designated for saturation determination is prepared for immediate analysis by chipping off the periphery—which, in more permeable cores, is severely contaminated by drilling fluid—with a hatchet, hammer, chisel, or knife. If cores are drilled or sawed prior to the saturation determination, the use of any cooling liquid during the cutting may cause both total liquid content or fluid-distribution data to be of doubtful significance. Cylinders and cubes for porosity and permeability determinations are cut with diamond drills and diamond or carborundum saws. The preferred sample sizes are:

a. Cylinders — ¾-in. to 1½-in. OD; minimum length to diameter ratio equals 1.
b. Cubes — ¾-in. minimum.

Usually cylinders are cut parallel to the bedding plane. Some laboratories prefer the use of cubes, as both horizontal and vertical permeabilities can be determined in each cube. Fragile cores may be shaped with a knife.

When cutting a plug, it is common practice to keep the sample wet with a cooling liquid to prevent fine cuttings from plugging the porous surfaces. The use of diesel oil or kerosene rather than water may be preferred as water will cause some types of core materials to swell, causing the sample to become fractured or to disintegrate.

Particular attention must be given by laboratory personnel to the identification of each laboratory sample prepared to assure that each foot of sample received by the laboratory is analyzed.

3.12 CLEANING OF SAMPLES

3.121 Solvents

Prior to the laboratory measurement of porosity and permeability, the original liquids must be completely removed from the core sample. Various solvents used for hydrocarbon-extraction purposes are listed alphabetically.

a. Acetone
b. Benzene
c. Benzene-methylalcohol
d. Carbon tetrachloride
e. Chloroform
f. Ethylene dichloride
g. Hexane
h. Naphtha
i. Tetrachloroethylene
j. Toluene
k. Trichloroethylene
l. Xylene

The particular solvent to be used should be selected in order not to attack, alter, or destroy the structure of the sample. It should be recognized that the solvents in this list may not be complete solvents for all hydrocarbon constituents in natural cores, but they have been widely used for extracting samples for routine analysis. Some will be more suitable than others for specific uses; e.g., chloroform has been found to be excellent for many mid-continent crudes, and toluene has been found useful for asphaltic crudes. Carbon tetrachloride may hydrolyze during extraction, forming hydrochloric acid as a product. When subjected to higher temperatures, it decomposes, liberating phosgene gas and leaving an insoluble material in the core.

Closed-type electrical heaters should be used whenever inflammable solvents are used. Safety precautions such as adequate ventilation of the laboratory, accessibility of fire extinguishers, fire buckets, and safety showers should always be observed. Extraction should be conducted under hoods equipped with forced-draft ventilation.

The various solvents used for extracting core samples can be reclaimed by well-known physical and chemical methods. Such recovery can make practical the use of an expensive solvent, which may be ideally suited for a particular extraction.

Salt can be removed by the use of methyl alcohol or other solvent in which salt is somewhat soluble. The presence of much salt in the cleaned and dried sample may affect the measured and porosity and permeability values. Consequently, core samples containing a formation water with high salinity, may require additional extraction to remove salt.

3.122 Flushing by Direct Pressuring of Solvent

Extraction of hydrocarbons and salt from reservoir rocks can be achieved by injecting one or more solvents into the core sample under pressure at room temperature. The pressures used are dependent upon the ability of fluids to move through the sample and may range from 10 to 1,000 psi. The core samples may be held in a rubber sleeve or suitable core-holding device which will permit the flow of solvent through the matrix of the sample. The volume of solvent required to completely remove hydrocarbons in the core sample is dependent upon: *a*. the nature of the hydrocarbons present in the sample; and *b*, the solvent or solvents used. The core is considered to be clean when the effluent solvent is clear. In some instances, more than one solvent may be required to remove heavy, asphaltic-type crude oils.

3.123 Flushing by Centrifuge[5]

A centrifuge with a specially designed head is used to spray warm, clean solvent (from a still) against the core samples. The centrifugal force causes solvent that contacts the samples to flow through them, thus displacing and extracting the oil (and water). The speed of rotation is varied from a few hundred to several thousand revolutions per minute, depending upon the permeability and degree of consolidation of the core samples being extracted. Samples up to 1½ in. in diameter and 3 in. in length can be successfully extracted by this method. Most common solvents can be used. The apparatus and procedure are described in 3.51.

3.124 Gas-driven Solvent Extraction

(U. S. Patent 2,617,719)

In this method of cleaning core samples, the core is subjected to repeated cycles of internal dissolved- or solution-gas drive until the core is cleaned of residual oil. The remaining solvent and water are removed by means of a drying oven.

When a core from an oil-bearing formation is brought to the surface and depressured, the gas dissolved in the oil comes out of solution and pushes some of the oil and water out of the core. This leaves the core sample with some of the pore space filled with gas at atmospheric pressure. The gas-filled space is the factor which makes it possible to remove the residual oil from the core. The gas-filled space in the core can be almost completely filled with solvent by surrounding the core with a suitable solvent containing a dissolved gas and applying sufficient hydraulic pressure. Under this condition, the solvent mixes with the oil in the core and subsequent depressuring to atmospheric pressure removes some of the residual oil.

If this cycle is repeated a sufficient number of times, the core becomes practically oil-free. The remaining solvent and water are then removed by vaporization. This method will clean any porosity, regardless of the type or complexity. It works in a crack or fissure system as well as in a pure intergranular-type porosity. It is successful in the so-called dead-end or one-opening type of porosity. It should be noted that this process may separate or fracture loosely consolidated core samples during cleaning.

Carbon dioxide gas is excellent because of low fire or explosion hazard and high solubility in most solvents. Some of the solvents which can be used are naphtha, toluene, or mixtures of solvents. With certain types of crude oil, cleaning time may be reduced if the core chamber is heated by a water bath, steam bath, or by electric heaters. One successful application of this method for routine cleaning of cores uses carbon dioxide and toluene at 200 psig with a hydraulic pressure of 1,000 psig. Cycles of approximately 30 min are used. The apparatus and procedure are described in 3.52.

3.125 Distillation-Extraction Method

The usual Soxhlet extraction apparatus, using a solvent or solvents which will dissolve and extract the oil and salt-laden water efficiently and not attack the sample, is suitable for the purpose of cleaning core samples. Extraction can be arranged in a manifold so that the oil and water-laden solvent siphons from each extractor into a common still from which fresh solvent is continuously distilled, condensed, and again distributed to the several extractors.

The cleanliness of the sample is best determined from the color of the solvent which siphons periodically from the extractor. Extraction should be continued until the extract is water-white. A non-luminescence of the extract under fluorescent light is a good criterion of complete extraction of the oil for a given solvent. It should be noted that the complete extraction of certain oils from core samples may require more than one solvent, and the fact that one solvent is water-white after contact with the sample does not necessarily mean that the oil has been completely removed from the sample. Descriptions of suitable apparatus and procedures may be found in most standard reference books on physico-chemical measurements. Details of one apparatus and procedure may be found in 3.55.

3.13 DRYING

Conventional core samples can be dried by:

a. A conventional controlled-temperature oven utilizing a maximum temperature of 240 F. for a minimum of 2 hours.

b. A vacuum controlled-temperature oven utilizing a maximum temperature of 200 F. for a minimum of 2 hours.

Each core sample should be dried until the weight becomes constant.

3.14 PRECAUTIONS

There are a number of precautions which must be observed in the preparation of all types of samples for routine core measurements. These are:

a. Samples containing clays and gypsum must not be dehydrated during preparation. Care must be exercised in drying samples containing hydrated or hydratable materials. In some cases, temperatures lower than those indicated in 3.13 must be used to prevent the dehydration of clays and gypsum.

b. Samples must be protected from erosion by the drip of the clean solvent when utilizing the Soxhlet extraction technique.

c. Care must be exercised in the selection of an extraction technique which does not physically damage samples which are not well-consolidated. The Soxhlet extraction technique is usually more suitable for this type of sample.

d. The usual criterion for sample cleanliness is a clean extract; but it must be recognized that many solvents are not complete solvents for all types of oils.

e. Samples containing heavy asphaltic oils usually require the cycling of more than one solvent.

3.2 FLUID-SATURATION DETERMINATION

Accurate determination of the fluid content and specific fluid saturations of cores is an important element in the interpretation of core-analysis data. Proper care in handling and preservation of the core until analyzed is very necessary to prevent changes in fluid content by drying or contact with water.

Specialized analytical techniques have been developed for the study of core samples of different physical characteristics and different sizes, as obtained by the various methods of coring. Several widely used procedures for determining core fluid saturations provide acceptable data.

3.21 RETORT METHOD AT ATMOSPHERIC PRESSURE

(Use of downdraft retort covered by U. S. Patents 2,282,654 and 2,361,844)

3.211 Principle

In conventional analysis the liquid saturations may be obtained by distillation of a sample at atmospheric pressure. This process is known as the retort method. Liquids in the sample are vaporized in the heating chamber, the vapors are condensed in a water condenser, and the recovered liquids are collected in calibrated receiving tubes. Representative pieces of core with an aggregate weight of between 100 and 175 grams are normally used in each retort sample.

3.212 Data

By using an oil correction curve, the accuracy of the oil value obtained by the retort method is within ±5 percent, and the reproducibility is within ±2 percent of the volumes measured. The accuracy of the water value obtained by this method is within ±2.5 percent of the volume measured. The oil and uncombined water distilled from each sample are calculated as percentages of bulk volume, using the total weight of the sample and the natural density determined on an adjacent piece of sample. The retort is a rapid method for measuring liquid content and is accurate enough for most applications of data.

3.213 Advantages

a. Liquid content is determined on large amounts of core sample.

b. The volume of each liquid recovered is obtained by direct measurement.

c. Possible error from the weight of salt deposited from water contained in the sample is eliminated.

d. Possible error from loss of sand grains in handling is eliminated.

e. Oil content is measured directly; whereas, in extraction methods, oil content is calculated by difference between relatively large numbers, where errors such as pointed out in c. and d. could cause large errors in calculated oil saturation.

3.214 Limitations

a. Water-calibration data for each formation are necessary for accurate results.

b. Accuracy of water-saturation data for samples containing clay materials is less because of difficulty in establishing correct retort temperature or time to remove uncombined water only.

c. Oil-recovery correction curve is required.

d. Two separate pieces of core are used to obtain the data.

The details of the apparatus and procedure may be found in 3.53.

3.22 VACUUM DISTILLATION METHOD

3.221 Principle

The vacuum distillation method for determining the oil and water content of a core consists of heating the core in an evacuated chamber, condensing the liberated vapors, and recording the volume of the recovered liquids. The procedure is applicable to cores of any size, but the apparatus described herein is designed for distillation of liquids from core samples approximately 1 in. in diameter and a maximum of 4 in. in length.

If the oil originally in the core contained components which were not distilled, a correction must be applied to the volume of the oil collected in order to estimate the volume of oil originally in the core. The correction factor may be determined experimentally by the distillation of a known volume of the oil.

3.222 Advantages

a. Oil and water content are measured directly and independently of each other.

b. Water content can be determined accurately with this technique if the core minerals are stable up to 446 F. (230 C.).

c. If the minerals are stable up to the temperatures used, the sample is not destroyed.

d. Oil-content determinations are very accurate where high-gravity crude oils are being distilled.

3.223 Limitations

a. Oil-content correction data must be determined for any oil other than high-gravity crude oils.

b. Low-gravity crude oil is difficult to distill at the temperatures used.

c. Close attention is often required during the distillation.

The apparatus and procedures are described in 3.54.

3.23 DISTILLATION-EXTRACTION METHOD

3.231 Principle

The distillation-extraction method of determining fluid saturations of cores depends upon distilling water from the sample, condensing it, and accumulating it in a calibrated receiver. The oil is removed by solvent extraction and is determined as the difference between the weight loss during the distillation-extraction operation and the weight of the accumulated water. The solvent used for extracting the oil normally has a boiling point above that of water, so that the water within the core is distilled out as it is heated by the solvent vapor. The solvent vapor condenses and continually drips on the core sample to extract the oil.

3.232 Data

The liqiud content of a core sample shall be reported to the nearest percent of the pore space, e.g., 22 percent oil and 43 percent water.

3.233 Advantages

a. The procedure is simple and requires little attention during the distillation.

b. Very accurate water-content determinations can be made.

c. Relatively low temperatures are normally used and the decomposition of minerals is minimized.

3.234 Limitations

a. Gain of water affects calculated oil content.

b. Loss of sand grains affects calculated oil content.

c. Proper drying temperature is critical because high heat causes loss of clay water, and low heat leaves residual solvent in the core. Both of these factors affect the calculated oil content.

Details of the apparatus and procedure may be found in 3.55.

3.3 POROSITY DETERMINATION

Porosity, which is defined as the ratio of the void-space volume to the bulk volume of a material, is an intrinsic property of all reservoir rocks. The amount of void space which can be occupied by hydrocarbons or water in a reservoir must be known for any intelligent estimate of the economics of oil or gas production. The precision with which porosity can be determined is largely a function of the methods used in its measurements. However, the results of porosity measurements by whatever methods are now in use cannot be expected to correspond exactly to *in situ* conditions owing to: *a*, possible relaxation of cores upon release of overburden and fluid pressures; and *b*, the hydraulic and mechanical actions of the coring process. Several logging tools using either electrical, nuclear, density, or sonic methods are used for porosity resolution around the well bore. The measurements obtained are, of course, calibrated against porosities measured at surface conditions and the relationships developed apply only to those surface conditions.

In moderate- to high-porosity rocks, most errors introduced in measured porosity values (unless extreme) either by method used, relaxation, or hydraulic or mechanical action are not of prime concern, since they have a relatively small effect percentagewise on the volumetrics of the reservoir. This is not true in low-porosity rocks, however, since a relatively small error here has a very appreciable effect percentagewise on the calculated pore volume.

In the laboratory usually one or two types of porosity are measured, viz., effective porosity or total porosity. Effective porosity, which is a measurement of the inter-connected voids, is derived from either bulk volume and apparent grain volume determinations or a direct measurement of the inter-connected void space. The measured volume of the inter-connected void space may vary with the method used. Total porosity, as the term implies, is a measure of the total void space in the rock sample and is determined by bulk-volume, dry-weight, and grain-density measurements. Inasmuch as some porosity logging devices respond to total porosity *in situ*, calibration of the response of those devices against laboratory total porosity should be preferable to calibration against effective porosity—possibly measured under a variety of conditions. Again, in moderate- to high-porosity rocks there is little significant difference between effective and total porosities since in such rocks most pores are well inter-connected. In low-porosity rocks, however, a very appreciable and significant difference sometimes is observed as a result of the restricted inter-connection of the pores.

Porosity, measured in a formation sample containing inter-granular clays, is subject to appreciable error regardless of porosity range. This error may be a result of shrinking of clays during the analysis, chemical changes within the clay, or flushing of the clay particles during coring operations. Very special handling and specific techniques should be developed for analyzing such formations.

Another facet of porosity measurement, which in fact applies to the entire field of core analysis, is the selection of conventional analysis vs. full-diameter analysis. The decision as to which type should be used would ideally be based entirely upon the homogeneity of the formation being analyzed. Most sandstones are sufficiently homogeneous that a small sample can be considered representative of the analysis increment. On the other hand, when the formation is heterogeneous as to pore structure or lithology, such as in vugular or fractured carbonates or thinly laminated sands and shale, full-diameter core techniques are more applicable. Therefore, the size of sample required to adequately represent the pore structure and lithology of the analysis increment should control the type of analysis used.

3.31 BULK-VOLUME MEASUREMENT

A measure of the bulk volume of a rock sample is required to determine the porosity of that sample. Bulk volume can be determined by several methods. The techniques included are: *a*, liquid displacement; *b*, caliper measurements; *c*, buoyancy; and *d*, grain density. Precautions to avoid trapping air around or under the sample, particularly if an irregular-shaped piece is selected, should always be taken when using the liquid displacement or buoyancy technique.

The sample selected for the porosity measurement should preferably be 10 to 20 cc in bulk volume. Normal sample shape and size is either: *a*, a right cylinder, ¾-*in* to 1½-*in*. OD, with length of at least 1 in.; or *b*, a cube of about ¾-in. side length. Irregular shapes may be used with proper precautions if samples of regular dimensions cannot be obtained.

3.311 Mercury Displacement

3.3111 Principle

A dried core sample is immersed in mercury in a calibrated pycnometer. The volume of mercury displaced by the sample is weighed. The measurement by weight can be repeated within ±0.02 cc if no air is trapped by the sample and the temperature remains constant. The measurement by volume can be repeated to ±0.05 cc.

3.3112 Advantages

a. Samples can be used for subsequent tests if no mercury penetration occurs.

b. The method is accurate if careful technique is used and precise measurements are made.

3.3113 Limitations

a. This method is slightly more time-consuming than some others for determining bulk volume.

b. Trapping air around the samples will create errors.

c. Samples with a vugular surface must be sealed by coating or filling the vugs to prevent mercury penetration. The volume of any coating must be subtracted from the total bulk volume measured. The apparatus and procedure are described in 3.56.

3.312 Bulk-volume Meter

3.3121 Principle

The bulk volume of core samples is measured by direct displacement into an inclined calibrated tube with a suitable scale. The liquid is displaced into the inclined tube by submerging the core sample under mercury in an adjacent, connected chamber. The apparatus is illustrated in Fig. 3.57F1.

If the meter is properly calibrated, readings should be reproducible within ±0.05 cc.

3.3122 Advantages

a. The equipment occupies a small space, is portable, and can be designed to accommodate small or large cores.

b. Calibration and operation are simple and quick.

3.3123 Limitations

a. Friable samples may contaminate the mercury and induce a small amount of error.

b. Vugular samples may retain small amounts of mercury which, again, induces error.

c. Trapping air around the sample will create errors.

The apparatus and procedure are described in 3.57.

3.313 Mercury Pump

3.3131 Principle

Mercury is pumped around the core sample which is enclosed in a calibrated steel pycnometer. The steel pycnometer is an integral part of the pump, which consists of a measuring cylinder (filled with mercury) and a metering plunger. A scale and dial arrangement, which is graduated to 0.01 cc, permits a reading of the movement of the plunger. The pycnometer is closed by a top which contains a small recessed opening. With no sample in the apparatus, the top is placed on the pycnometer and the pump plunger is advanced until a small bead of mercury appears at the opening of the top. The pump scale is then set on zero. After backing off the plunger to lower the mercury in the pycnometer, the sample is inserted, and the plunger is again advanced until a small bead of mercury appears at the opening. The reading on the scale and vernier arrangement is taken, and the difference between this reading and the first reading (instrument zero) is the bulk volume of the sample.

The measurement can be reproduced to ± 0.01 cc if the pump is rezeroed for each sample.

3.3132 Advantage

a. This procedure allows very rapid measurements to be made.

3.3133 Limitations

a. Trapping air around the sample will create errors.

b. Vuggy samples or extremely high-permeability samples may be penetrated by the mercury which will result in low values.

The apparatus and procedure are described in 3.5.14.

3.314 Caliper

3.3141 Principle

Samples which are right cylinders or other regular shapes may be calipered to obtain bulk volume. A micrometer or vernier caliper, which can be read to the nearest 0.01 cm, can be used.

The length and diameter of the cylinder, or the sides of the cube, are measured several times in each dimension to define any irregularities in the shape. Small deviations in the shape may be averaged out. The cross-sectional area of the sample is calculated from the diameter or the side width and breadth measurements on shaped pieces and multiplied by the length to obtain bulk volume.

Volumes can be repeated to ± 0.15 cc.

3.3142 Advantages

a. The sample may be used for other tests.

b. The procedure is rapid.

c. Accurate values can be obtained if samples are true regular shapes.

3.3143 Limitation

a. Samples with irregular shapes cannot be measured by this method.

3.315 Buoyancy

3.3151 Principle

The sample is saturated with a liquid of known density, such as kerosene. Excess liquid is removed from the sample and the saturated sample is weighed. A beaker is filled with the saturating liquid, and the saturated sample is submerged in it. The sample is supported by a fine wire attached to the stirrup of the balance and a submerged weight measurement is made. The net submerged weight is obtained by subtracting the tare weight from the measured submerged weight. The initial weight of the saturated sample in air minus the weight when submerged, divided by the density of the saturating liquid yields bulk volume.

3.3152 Advantages

a. Accurate values can be attained if proper technique is used.

b. The sample is saturated with liquid for other tests which may be desired.

3.3153 Limitations

a. Samples must be completely saturated to eliminate buoyancy effects.

b. The liquid must be removed for some other tests which may be desired.

c. Cores containing vugs cannot be measured by this method.

d. Liquids which may leach the sample or cause swelling of the matrix cannot be used.

The apparatus and procedure are described as part of 3.5.13.

3.32 PORE-VOLUME MEASUREMENT

The pore-volume measurement may be made either as *a*, total pore volume on a crushed sample; or as *b*, effective pore volume on the uncrushed core.

3.321 Total Pore Volume

The total pore volume is the difference between the bulk volume and the grain volume. An accurate grain-density measurement is necessary for calculating the grain volume from the weight of the sample. In heterogeneous core samples, great care should be taken to obtain representative portions of the core for grain-density measurements.

3.3211 Dry Method for Grain Density

3.32111 Principle

The weighed sample is placed in a Boyle's Law porosimeter used to measure grain volume. Its grain density is determined as described in 3.58. The grain density is used to calculate the percent total porosity of the original saturation sample by subtracting the volume of the sand grains from the bulk volume. The procedure should be reproducible to within ± 0.5 of 1 porosity percent, provided the bulk volume measurement is equally precise.

3.32112 Advantages

a. This method is faster than the "wet method".

b. No liquids are involved in the measurement and the sample can be retained for future reference.

c. The saturation sample may be used for this test.

d. The equipment is easy to operate.

e. The procedure has excellent repeatability.

3.32113 Limitations

a. The accuracy will be affected by shaliness in the sample.

b. The grain density obtained is not a direct measurement of the entire sample.

For further details, see 3.58.

3.3212 Wet Method for Grain Density

3.32121 Principle

A portion of a weighed crushed extraction sample (bulk volume is measured prior to pulverizing) is used to displace an equivalent volume of liquid—e.g., toluene—in a volumetric flask. This displaced volume is determined; and knowing the weight of the core sample, the grain density may be calculated from the relationship:

Density = weight of sample/volume of sample (1)

The reproducibility should be the same as that for the dry method (3.3211).

3.32122 Advantage

a. Many samples can be handled at one time.

3.32123 *Limitations*

a. The grain density obtained is not a direct measurement of the entire sample.

b. If the wetting action is not effective, some error may be introduced.

c. The liquid used (particularly if it is not highly refined and perhaps even then) may react with shale or other minerals present in the rock.

For further details see 3.59.

3.322 Effective Pore Volume

The measurement of the effective porosity of reservoir rocks can be made by determining the volume of sand grains in a core sample by a procedure depending on Boyle's Law or by procedures based on measuring the void volume.

3.3221 Grain-volume Measurement

3.32211 Boyle's Law Single-cell Method

3.322111 Principle

The effective pore volume is measured by compressing a known volume of gas at a known pressure into a core which was originally at atmospheric pressure. The sand grain volume and pore volume are calculated from these pressure measurements. The grain volume is defined as the difference between the total gas space of the void volume plus the annulus and the calibrated volume of the core holder. The void volume of the core is obtained by subtracting the measured grain volume from the bulk volume. This void volume is the effective pore volume of the core.

Grain-volume measurements should be reproducible within ±0.01 cc using Boyle's Law single-cell units.

3.322112 Advantages

a. The test specimen is not damaged in any way and can be used for other measurements.

b. The operation is quick, simple, and has excellent repeatability.

3.322113 Limitations

a. For good accuracy, extremely careful calibration is required.

b. Changes for temperature and barometric pressure must be corrected.

c. The measured value may be higher than the true porosity value if gases absorb on the core surfaces. The use of helium will minimize this possibility.

For apparatus and procedural details of one Boyle's Law single-cell unit see 3.5.10.

3.32212 Boyle's Law Double-cell Method

3.322121 Principle

The sand grain volume is measured in an apparatus consisting of two connected chambers. The core sample is placed in one chamber and the gas pressure in this chamber is adjusted to some known value. The gas in the second chamber is adjusted to some different known pressure. The pressure is equalized and measured and the final volume is known. From these data and Boyle's Law, the volume occupied by the sand grains is calculated. The pore volume is the difference between the grain volume and the bulk volume.

Three modifications for Boyle's Law double-cell apparatus and procedure are described in 3.5.11. Modification A gives grain-volume values from 4.0 to 13.5 cc with errors that continually decrease in this range from ±1.1 percent to ±0.02 percent of the calculated pore volume measured. Other users also report this order of accuracy. Any of the Boyle's Law double-cell porosimeters discussed should be capable of this accuracy when properly built and operated.

3.322122 Advantages and Limitations

The same points apply here as for Boyle's Law single-cell (3.322112 and 3.322113).

3.3222 Void-volume Measurement

3.32221 Washburn-Bunting Method[6]

3.322211 Principle

The effective pore volume is measured by expanding the pore gas and measuring its amount. This method employs simple equipment (Fig. 3.5.12F1) and applies best to well-consolidated cores. The bulk volume of the core must be measured independently.

Measurements are reproducible to ±1.0 porosity percent in the porosity range of 8 to 40 percent.

3.322212 Advantage

a. A simple, rapid operation.

3.322213 Limitations

a. Repeated expansions are necessary for samples with very low porosities and permeabilities.

b. When applied to friable or highly permeable cores, this method gives rise to troublesome mercury penetration into the cores, rendering them useless for further tests.

c. This apparatus is susceptible to leakage around the stopcock.

The apparatus and procedure are described in 3.5.12.

3.32222 Summation of Fluids
(U. S. Patent No. 2,345,535)

3.322221 Principle

The pore spaces of core samples normally contain some gas, as a result of the liberation and expansion of dissolved gas as the core and its reservoir-fluid content are brought to the surface. The remaining pore space is filled with liquid, either water or both oil and water. One method of obtaining porosity involves determining independently the gas, oil, and water contents of the core, each being measured as a percentage of the bulk volume of the core. The sum of these three percentages is equal to porosity. This procedure requires that the core sample be divided into two portions, care being taken to select adjacent portions with similar characteristics. One portion, a single piece of 25- to 40-gram size, is used to determine the gas content by injecting mercury into the sample at 750 or 1,000 psi. The second portion, which may be composed of several pieces with a total weight of 100 to 175 grams, is used to determine the oil and water content.

The porosity determination is normally within ±0.5 porosity percent.

3.322222 Advantages

a. Measurements are made on large amounts of core sample.

b. Volume of each fluid is obtained by direct measurement.

c. No error arises as a result of salt deposition from water content of sample or loss of sand grains in handling.

3.322223 Limitations

a. Some error may be introduced by inability to account entirely for water of hydration.

b. Two separate pieces of core are used to obtain the data.

The apparatus and procedure are described in 3.53 and 5.512.

3.32223 *Hydrocarbon Resaturation*

3.322231 Principle

The measurement of effective porosity by the hydrocarbon liquid resaturation technique involves the gravimetric determination of pore volume (and bulk volume) by obtaining: *a*, the weight of the core sample clean and dry; *b*, the weight of the sample saturated with a liquid of known density; and *c*, the weight of the saturated sample submerged in the liquid of known density.

The determination of effective porosity by the hydrocarbon resaturation technique must of necessity be limited to samples which can be saturated and the saturated weight successfully determined. Experience has shown that the porosity of vugular and cavernous limestone cores cannot be accurately determined by this method because of the loss of liquid during the weighing process.

This method should give effective porosity within ±0.5 porosity percent.

3.322232 Advantages

a. Many samples can be handled at one time.
b. The procedure is basically very accurate.

3.322233 Limitations

a. The procedure is slow in regard to total elapsed time of measurement. The amount of "operator time" is reduced from some of the procedures for other methods.

b. Special precautions are necessary to insure complete saturation.

The apparatus and procedure are described in 3.5.13.

3.32224 Mercury Pump Method
(U. S. Patent No. 2,874,565)

3.322241 Principle

According to Boyle's Law of isothermal expansion, when the pressure on a gas is reduced to half the original pressure, the volume of the gas is doubled. The mercury pump, which may be adapted to utilize this principle, provides a fast and accurate procedure for measuring the porosity of samples that have been extracted and dried.

Porosity determinations can be made by this procedure with errors not exceeding ±0.4 porosity percent.

3.322242 Advantages and Limitations

The advantages and limitations which apply to the Boyle's Law single-cell method apply here as well (see 3.32211).

The description of the apparatus and procedural details may be found in 3.5.14.

3.4 GAS PERMEABILITY DETERMINATION

Permeability is a measure of the ability of a porous sample to transmit fluids. Either gases or liquids are used as fluids in permeability measurements. However, liquid permeabilities are not considered routine because of such factors as interaction between rock constituents and liquids and control of bacterial action. Therefore, only gas permeability will be considered in this manual of routine practices.

The permeability measurement will be standardized using dry air as the gas. If air permeabilities reported for routine core analysis have been corrected, using a standard table of Klinkenberg corrections,[7] then this should be noted specifically in the report. This corrects the gas permeability of a porous medium to the corresponding value for a non-reacting liquid. This correction is most important for samples with low permeability. The direction parallel to the bedding plane will be standardized as the horizontal permeability. Any measurements in other directions—i.e., vertical—should be so specified and the details described.

Samples of hard, consolidated cores having uniform properties are cut to shape and their permeability measured directly by conventional methods. A proper frequency of samples must be measured to obtain a representative permeability for the rock. Friable, soft, or shaly cores may require support to prevent distortion or alteration during testing for permeability. Such samples may be supported by mounting in a suitable potting plastic or optical pitch. Friable or soft samples supported in this way are then run according to the conventional core-analysis scheme.

Vugular, fractured, or crystalline carbonate rock, fractured and recemented cherts, and laminated shaly rocks are often handled by full-diameter methods to obtain a more representative permeability value for the interval analyzed.

3.41 GENERAL PROCEDURE

The sample used for the permeability measurements may be either the consolidated piece used previously for saturation and porosity determination, or a separate sample. If the sample has been used for saturation measurements, it is already clean. Otherwise it must be extracted and dried to remove the oil and water as described in the section on laboratory core preparation (see 3.1). Precautions to remove salt may be necessary if the interstitial water was very saline.

An air permeameter consists of the following major units (see schematic drawing, Fig. 3.5.15F1, of 3.5.15):

a. A source of dry air.
b. Pressure regulator.
c. Inlet-pressure measuring device.
d. Core holder. (Hassler and Fancher-type holders are used for conventional core analysis.)
e. Outlet-pressure measuring device.
f. A flow-rate metering device.

A standard permeameter should be designed to measure air permeabilities within a range of 0.1 to 5,000 md.

Because of the sensitivity of the permeability measurement to minor changes in sand lithology, measured values from adjacent pieces in an apparently homogeneous sand may not check within ±5 percent. For this reason any given measurement may not exactly characterize a given sand, and dictates the use of not more than two significant figures in reporting permeabilities.

Observation of the precautions listed in 3.5.15.3 and care in operating the equipment described there can lead to a reproducibility of about ±2 percent for most samples with permeabilities of 0.1 md or more.

3.5 DESCRIPTION OF PROCEDURES FOR ANALYSES

3.51 SOLVENT FLUSHING BY CENTRIFUGE[5]

3.511 Apparatus

The apparatus consists of two major parts, viz., a centrifuge and a solvent still.

The special centrifuge head required for this work may be put in certain types of commercially available centrifuges, or it may be installed in specially designed instruments. The head has a small-diameter circular trough at the center into which clean, warm solvent flows. The solvent is forced from the trough through small radial holes by centrifugal action. The holes are countersunk at the outward ends to cause the solvent to be expelled as a fine mist toward the outside ring of the head. The holes are spaced horizontally and vertically in a pattern to give good coverage to the core samples. The outer ring of the head holds the samples in position. Holes in the outer ring allow fluids to escape from the head. The chamber in which the head operates serves to collect the solvent and extracted fluids which then drain by gravity to the solvent still. The centrifuge chamber should be vapor-tight.

The boiler section of the still is normally of large capacity (about 10 liters). It should be heated with approximately 1,000 watts in order to supply a sufficient volume of clean solvent to the centrifuge. The heaters may be either external or immersion type. The boilers are normally well-insulated to improve the efficiency of the still. The condensing jacket and condensate trap are built as in a Soxhlet extractor so distilled solvent may be collected until it fills a siphon line, at which time the collected clean solvent siphons into the centrifuge and a new cycle is started. Heat from the boiling solvent keeps the solvent in the condensate trap warm until it is "dumped" into the centrifuge. A siphon bypass line will allow the continuous flow of solvent into the centrifuge, if desired.

The still is normally of such a height and is placed in relation to the centrifuge so that clean solvent may flow by gravity to the centrifuge, and dirty solvent may flow by gravity to the still boiler.

The centrifuge head and the still must be made of materials which will not react with the solvents used. Stainless steel is often used, but aluminum can be used in many applications. The still and centrifuge should be operated in an enclosed vented cabinet or hood.

3.512 Procedure

a. Turn on the solvent still heater and cooling-jacket water.

b. Place a strip of felt inside the outer ring of the centrifuge head. This strip is used to eliminate the "end effects" in the core samples and to cushion the edges of the core samples as they are forced against the rim of the rotating head.

c. Place one end of the core samples against the felt strip. Samples of like size and density should be placed opposite each other in the head in order to approach as nearly as possible balanced weight in the head. Visual observation will normally be sufficient to match samples for placement opposite each other. Weighing the samples is usually unnecessary because near-perfect balance is not required in the centrifuge. The centrifuges in use in this application have heavy flywheels or weight-balancing devices to compensate light unbalances in the load.

d. If the centrifuge is not loaded to capacity, distribute the samples around the head in order to distribute the load. The conditions of the foregoing step should still be observed. (A felt strip is sometimes placed around the inside ends of the samples to distribute the solvent.)

e. Close the centrifuge.

f. When the still starts to cycle solvent, start the centrifuge. Adjust the speed control to obtain the desired centrifuge speed. Slow speeds should be used for poorly consolidated material with little structural strength, and high speeds should be used for hard samples. Average speed should be about 3,000 rpm.

g. Centrifuge the samples until extraction is complete. A glass bowl or section in the solvent drain line allows a quick check of the cleanliness of the used solvent and thus a check on the degree of extraction attained. Normally ½ hour extraction time is sufficient to clean samples on which accurate air permeability measurements are desired. An extraction time of 2 hours is normally sufficient for any purpose.

h. Open a bypass valve to allow distilled solvent to return to the still boiler without going through the centrifuge.

i. Run the centrifuge without solvent for several minutes to partially dry the core samples.

j. Stop the centrifuge, and remove the core samples for oven drying.

3.52 GAS-DRIVEN SOLVENT EXTRACTION (U. S. Patent 2,617,719)

3.521 Apparatus

Fig. 3.52F1 is a diagrammatic sketch of one type of apparatus which is used to apply this cleaning method. It consists of a core chamber, a hydraulic pump, a solvent reservoir, and other miscellaneous items such as pressure gages and valves. Used solvent can be recovered, if necessary, by use of an auxiliary boiler and tower.

3.522 Procedure

The cores are placed in the core chamber through the open end. A cap containing an O-ring is screwed in place and the chamber pressured with gas to a pressure equal to the pressure of the gas dissolved in the solvent. The gas in the chamber is then displaced at constant pressure by the solvent-gas mixture. After the chamber is filled with the mixture, it

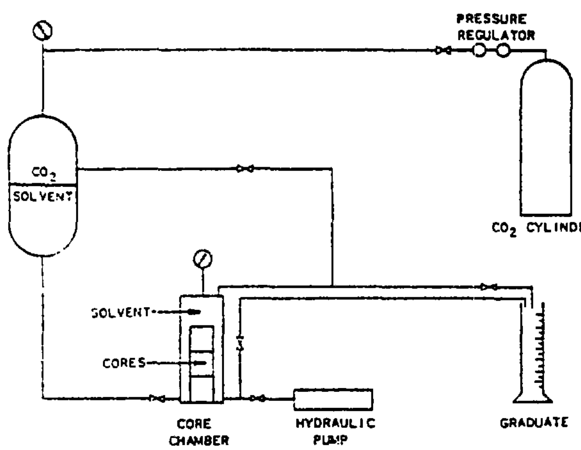


FIG. 3.52F1—SKETCH OF ONE TYPE OF APPARATUS USED TO APPLY CLEANING METHOD

is pressured by means of the hydraulic pump to approximately four or five times the solvent gas pressure. When liquid flow into the cores ceases, the core chamber is depressured rapidly to atmospheric pressure and the cores left submerged in the solvent until most of the gas has flowed from the cores. The solvent is then drained from the chamber and the cycle repeated.

3.523 Data

Data showing the number of cycles necessary to clean full-diameter cores for 4 different types of formations are presented in Fig. 4.51F1, which shows a plot of cleaning cycles vs. porosity for an intergranular-type lime, a fractured lime, a relatively clean sand, and a shaly sand. The core samples reported here were cleaned and dried and the porosity determined. They were then subjected to additional cleaning cycles and dried each time until the pore volume showed no increase. Fewer cycles may be required to clean corresponding conventional core samples. Additional discussion may be found in 4.122.

Consideration of the type of crude in the sample is important in determining the number of cycles necessary for cleaning. In any one type of porosity, a low-gravity asphaltic crude will require more cleaning cycles than a high-gravity crude.

3.53 RETORT METHOD AT ATMOSPHERIC PRESSURE

(Use of downdraft retort covered by U. S. Patents No. 2,282,654 and No. 2,361,844)

3.531 Apparatus

A single-unit type of retort is shown in Fig. 3.53F1. The sample is contained in a stainless-steel cup with a tight-fitting, screw-on top. The sample container cup is placed in an insulated electric heater. The outlet stem of the cup makes a vapor-tight seal with the top of the condensing tube. The condensing tube is fitted with an air-fin cooling section, and a chamber is provided for cooling water around a portion of the tube. A calibrated glass receiving tube collects the liquids.

A modified apparatus consists of an insulated oven made to accommodate several sample cups simultaneously, as shown in Fig. 3.53F2. The oven is heated with continuous wire or by rod-type heating elements, and the sample cups are arranged in the oven in such a manner that an equal amount of heat is supplied to each. The temperature of the oven may be controlled at any temperature up to 1,200 F. The outlet stem of each cup makes a vapor-tight seal with the top of the condensing tube. The condensing tube is a straight tubular condenser and is surrounded by a water bath beneath the oven section. A calibrated glass receiving tube collects the liquids from each condensing tube.

3.532 Procedure

When using the multiple-sample retort oven type, the procedure for obtaining the fluid saturations is as follows: A crushed core sample, weighed accurately and comprising 100 to 175 grams, is put into each sample cup and the cups are placed in the retort oven. The temperature control on the retort is set to a predetermined temperature. To determine the temperature required to retort the uncombined water from samples of a specific formation, a calibration graph of temperature vs. water recovery is plotted, as in Fig. 3.53F3. The first plateau on this curve is taken

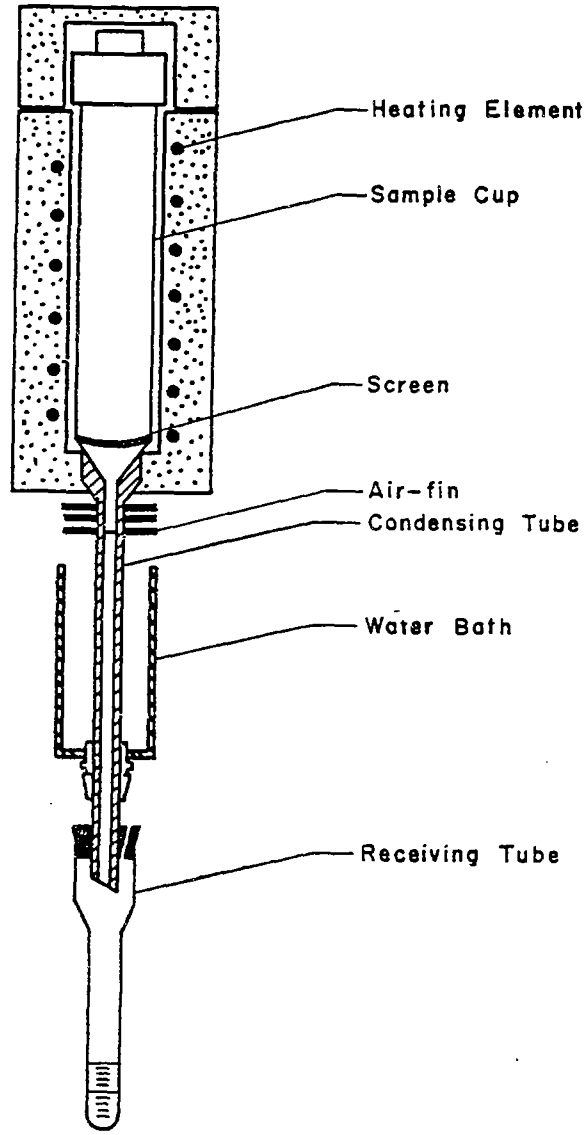


FIG. 3.53F1—OVEN RETORT—ATMOSPHERIC PRESSURE

as the temperature at which the uncombined water will be completely removed. Water removed at higher temperatures may result from the dehydration of hydratable minerals. The predetermined temperature setting used in the procedure is taken as the temperature value just above the plateau of this curve. *It is necessary to determine the proper temperature for each formation.* The temperature of the oven at the time the sample cups are inserted is not critical, provided it is below the predetermined temperature. After reaching the set temperature level, the sample is heated for approximately 20 min to vaporize the uncombined water. The water reading obtained is recorded.

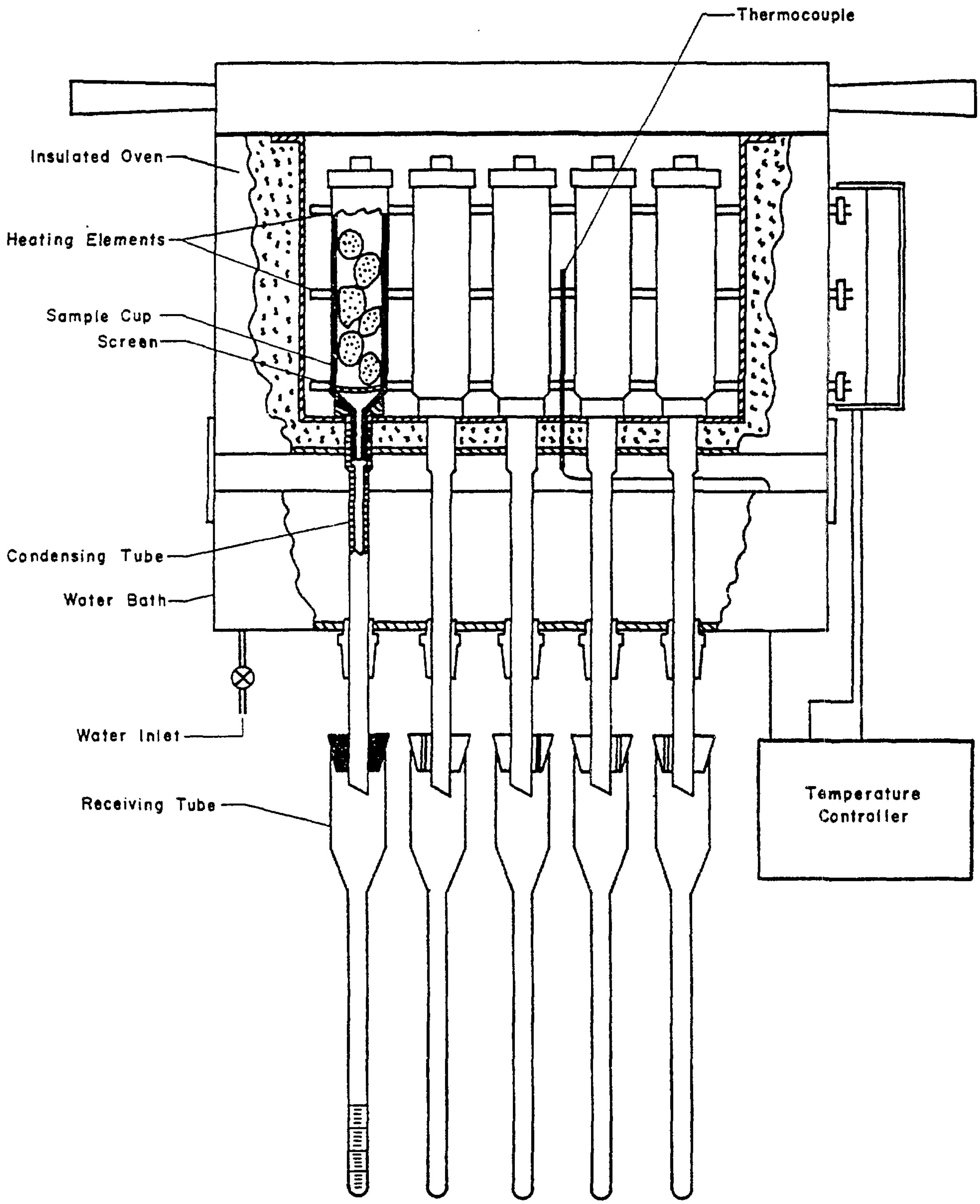


FIG. 3.53F2—OVEN RETORT—ATMOSPHERIC PRESSURE

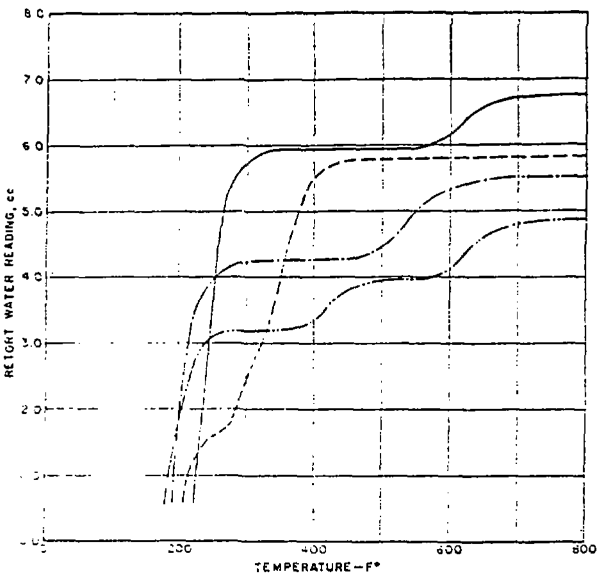


FIG. 3.53F3—WATER CALIBRATION CURVES

After the uncombined water reading is taken, the condensing water bath is drained to allow the condensing tubes to warm. The temperature within the retort is then raised to 1,200 F. to vaporize the heavier oil fractions. After 20 to 30 min of heating the sample at 1,200 F., the heater is turned off and the recovered oil volume is recorded. A correction is applied to the volume of oil collected in order to compensate for vapor losses, coking, and cracking of the oil. This correction is derived empirically from calibration tests made on each type of formation oil. (One example is shown in Fig. 3.53F4.)

Fig. 3.53F5 shows examples of water-distillation calibration curves obtained on different types of formations by an alternate procedure. The retorts are loaded and heat is applied continuously (without temperature control). The volume of water distilled, condensed, and recovered from the sample is plotted vs. the length of time of retorting. The first plateau, or the region from 12 to 20 min in Fig. 3.53F5, indicates removal of all uncombined water. The water reading taken on this plateau is recorded as free water. Curves of this type should be developed for each formation encountered.

3.533 Determination of Natural Density and Gas Content

The bulk volume and gas content of a representative, accurately weighed sample of 25 to 40 grams are determined in a specially adapted mercury pump. The pump shown in Fig. 3.5.14F1 can be used, or one similar to it but without the high-pressure valve or vacuum gage. The sample—still in its natural condition—is placed in the chamber of the volumetric mercury pump, and the bulk volume is measured to 0.01 cc by displacement of mercury. The sample weight is divided by bulk volume to obtain natural density. The needle valve in the cap of the sample chamber is closed and mercury is injected into the sample at 750 or 1,000 psi. The volume of mercury injected into the sample, measured to 0.01 cc, is considered a measure of the gas content. Gas volume is divided by the measured bulk volume to obtain the gas saturation expressed as a percentage of bulk volume.

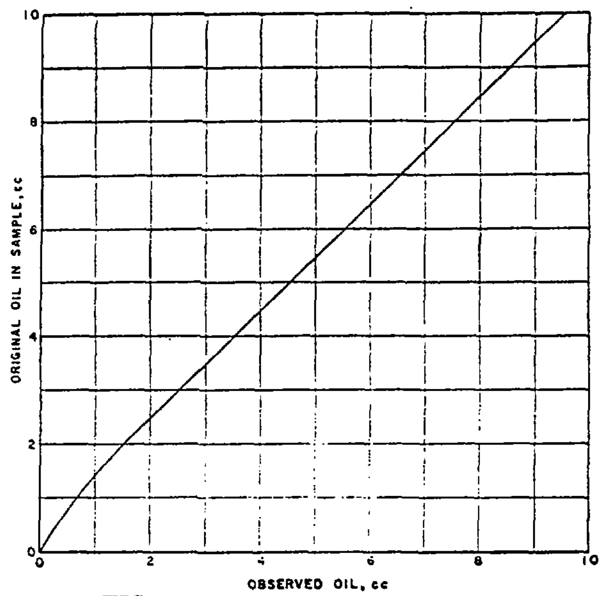


FIG. 3.53F4—OIL CALIBRATION CONVENTIONAL RETORT CUP

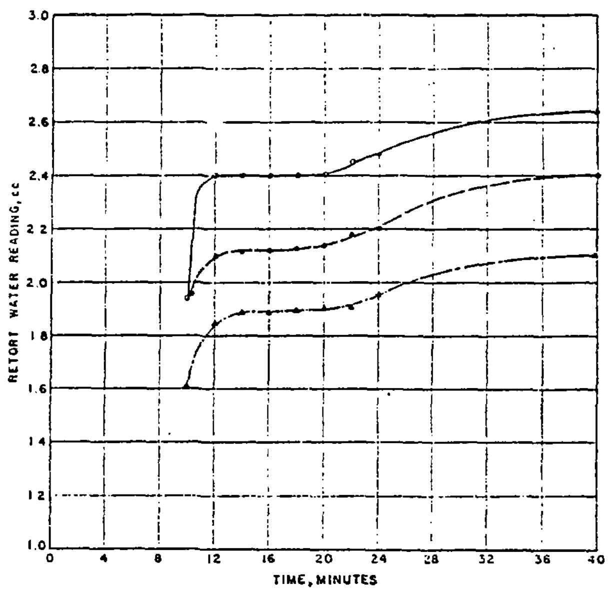


FIG. 3.53F5—WATER CALIBRATION CURVES

3.54 VACUUM DISTILLATION METHOD

3.541 Apparatus

The apparatus consists of an individual heating chamber, a calibrated condenser-collection tube, a vacuum source and manifold, and a liquid nitrogen container.

Fig. 3.54F1 shows the core heating chamber and vapor-condenser system. The glass chamber is encased in a 90-watt 115-volt asbestos-covered heating mantle. Current is supplied to the heating coils from a 110-volt a-c supply through a variable voltage transformer. Glass core supports are provided near the base of the chamber. The top of the chamber

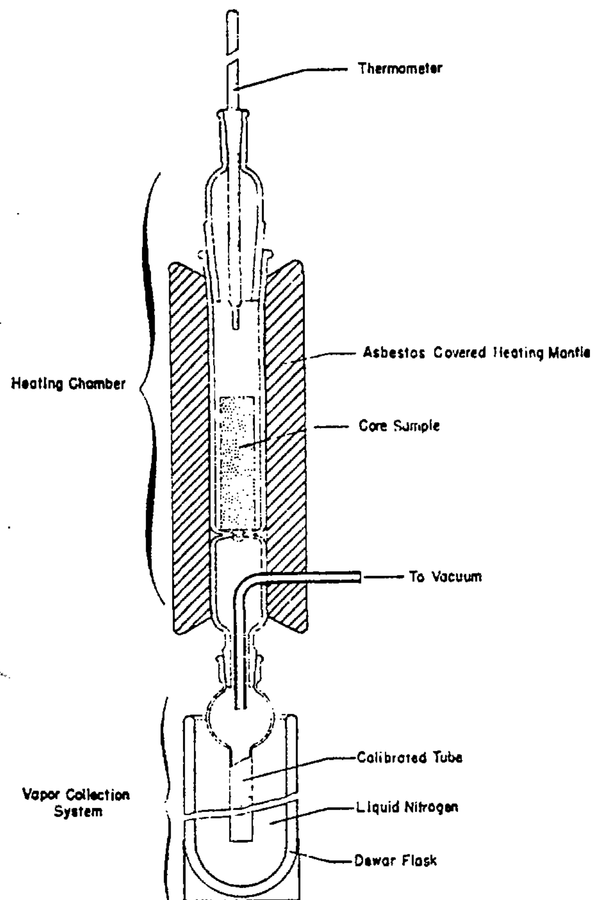


FIG. 3.54F1—CORE HEATING CHAMBER AND PRODUCT RECOVERY SYSTEM

is closed with a thermometer adapter. The temperature in the chamber is measured with a thermometer equipped with a ground-glass joint which permits it to make a vapor-tight seal in the thermometer adapter; a 10-360 C. thermometer (50-680 F.) with a 100-mm immersion length is commonly used. The bottom of the chamber is provided with a vacuum connection tube which extends ¾ in. into the condenser-collection tube, thus permitting the removal of non-condensable gases during distillation.

The vapor-collection tube is shown in Fig. 3.54F2. The liquids distilled from the core sample are frozen on the walls of the bulb of the collecting tube. A bulb diameter of 1½-in. is required to contain these frozen liquids. The graduated portion of the condenser tube is calibrated in tenths of a cubic centimeter to a total liquid volume of 10 cc. A vacuum manifold permits the vacuum distillation of several samples simultaneously. Two standard vacuum pumps, a fractionating oil diffusion pump, and a precise vacuum gage comprise the auxiliary equipment.

3.542 Procedure

The core sample is placed in the core chamber of the vacuum distillation apparatus. The ground-glass joints are lightly covered with high-vacuum silicone grease, and the apparatus is assembled as shown in Fig. 3.54F1. A flask containing liquid nitrogen is elevated to submerge the calibrated condenser tube until the liquid-nitrogen level coincides with the base of the glass vacuum tube extending from the bottom of the core chamber. The liquid nitrogen is kept at this level throughout the operation. The system is evacuated with two standard vacuum pumps until the pressure is reduced to about 0.1 mm of mercury. The fractionating oil diffusion pump is then opened to the system, and the pressure is reduced to less than 0.01 mm of mercury. Heat is applied to the core chamber by the external heater, with the temperature being maintained at approximately 446 F. (230 C.) during the distillation.

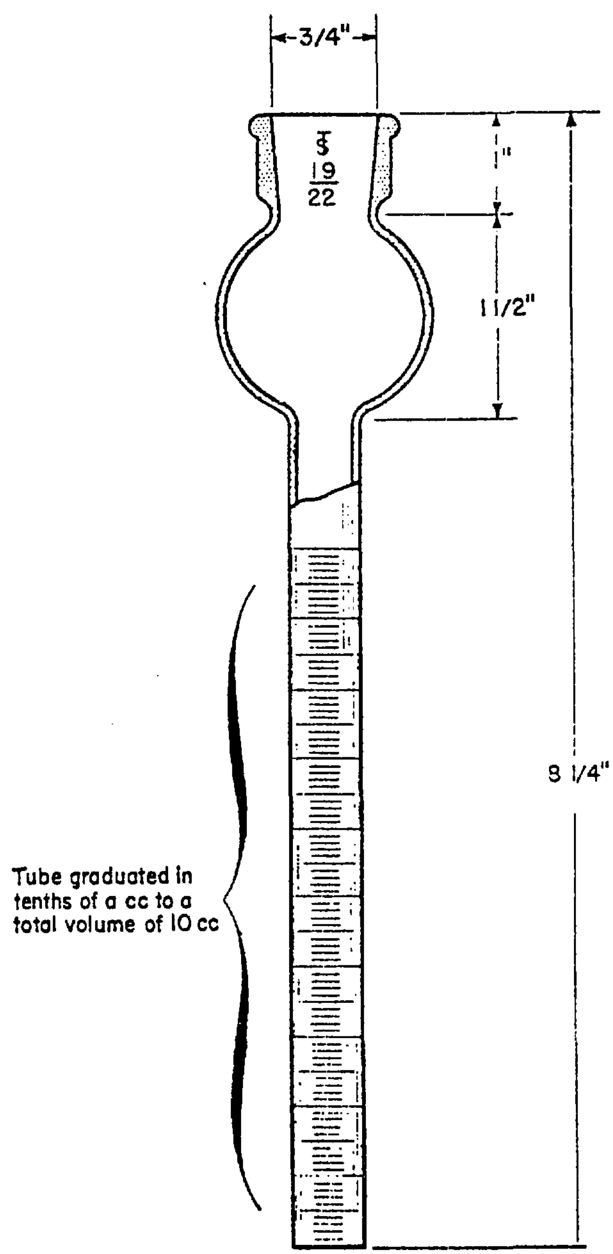


FIG. 3.54F2—PRODUCT CONDENSING AND RECEIVING TUBE

One hour after the core chamber reaches the operating temperature of 446 F. (230 C.) the vacuum is removed and the heat discontinued. The flask containing liquid nitrogen is lowered, the thermometer is removed, and the condenser tube is allowed to return to room temperature. When the liquids reach room temperature, the volumes of the liquids are recorded. If the water and oil are emulsified, it may be necessary to centrifuge the condenser tube to effect the separation of the liquids. It may be desirable to convert the volume of water distilled to the volume of the original salt solution. This is accomplished through the use of the following equation:

$$\text{Volume of original salt solution} = \text{volume of water distilled} \left(\frac{\text{density of distilled water}}{\text{density of original salt solution}} \right) \left(\frac{100}{100\text{—percent salt by weight in original solution}} \right) \quad (2)$$

3.55 DISTILLATION EXTRACTION METHOD

3.551 Apparatus

General: The apparatus consists of a pyrex glass flask or a metal still, heated by suitable means and provided with a reflux condenser that discharges into a trap connected to the flask or still. The trap serves to collect and to measure the condensed water and to return the solvent to the flask or still. An extraction thimble, in which the core is placed, is supported in the flask or still.

Glass Flask: The glass flask (Fig. 3.55F1) has a flat bottom, wide mouth, and a long neck, with indentations spaced evenly around the base of the neck to support an extraction thimble containing the core sample.

Metal Still: The metal still is a vertical cylindrical vessel 2⅝ in. ID, 9⅛ in. long. The top plate contains an O-ring seal. The glass trap return to the still contains a 28/12 ball-and-socket joint with clamp. The extraction thimble is supported in the still by a wire holder.

Trap: The glass trap (Fig. 3.55F1) has a graduated section marked in 0.10-ml divisions. It has a capacity of 5 ml and the graduated section is approximately 130 mm long. The return to the flask has a drip tip. Larger or smaller traps may be required for some cores containing unusual volumes of water.

Condenser: The condenser (Fig. 3.55F1) is a water-cooled, reflux, glass-tube type, with a jacket approximately 300 mm long and the straight inner tube approximately 10 mm in diameter. The bottom of the condenser has a drip tip.

Extraction Thimbles:

a. Coarse round-bottom alundum thimbles, approximately 34 mm inside diameter and 80 mm long, are used to hold the core samples. The rate of drainage from the thimbles may be increased by cutting small slots in the bottom and placing a pad of glass wool or cotton in the bottom. A pad of glass wool or cotton is placed on top of the core sample to protect the sample from the drip of solvent from the trap return.

b. As an alternate, a paper extraction thimble approximately 33 mm inside diameter and 80 mm long may be used. These thimbles are used with a glass-covered bottle during weighing operations to minimize the change in weight of the thimble resulting from absorption of water from the air.

Extraction Cups: If it is desired, extraction cups with a siphon may be used to hold the thimble within the flask for alternate immersion and drainage during the extraction.

Drying Oven: Following extraction, the sample may be dried quickly in a vacuum (approximately 29 in.) oven (see 3.13).

3.552 Procedure

The thimbles containing the core sample are weighed quickly and placed in the extractors. The samples are weighed to the nearest 0.01 gram.

The samples are extracted with a solvent which is kept water-free because extraneous water will give erroneous results. When the atmosphere is nearly saturated with water vapor, care should be taken to prevent condensation of atmospheric moisture in the condenser and subsequent collection in the trap. Water hangup in condenser and trap may be an appreciable error if the core sample contains a small volume of water. The hangup of water may be removed by pouring a small volume of solvent containing a detergent down the condenser tube. However, when detergent is added to the solvent in the trap, it causes the meniscus between the water and solvent to become more nearly flat. The correction required by the change in the shape of the meniscus may be determined by adding a known amount of water to the trap, then adding solvent and detergent. For 5-ml traps this correction is about —0.03 ml.

Extraction is continued until no more oil or water may be removed from the sample (2 to 3 hours for crushed material, 6 to 8 hours for consolidated material). Samples containing low-gravity crude oils or very small pore channels require longer extraction time. Low-gravity, high-asphalt content crude oils are generally difficult to extract. Some oils of this type may not be completely removed after 24 hours extraction. To obtain complete removal of the oil, it may be necessary to use more than one solvent.

The rate of extraction may be increased by use of a glass extraction siphon cup fitted within the flask. The effect of alternate immersion and drainage may be obtained also by extraction in apparatus equipped with a water trap, as described, and then followed by additional extraction in a Soxhlet extractor after the water has been removed.

After complete extraction the thimble is removed, dried, and weighed. The loss in weight of the sample represents the combined weight of extracted oil and water from the sample. The weight of the volume of water measured in the trap is subtracted from the total liquid weight to determine the weight of oil extracted from the core sample.

To express the water and oil contents as percent of the pore space in the reservoir rock requires, in addition to the foregoing information, the porosity of the rock (3.3), the bulk volume of the sample (3.31), and the specific gravity of the oil produced from the reservoir.

3.553 Drying after Extraction

a. *Heating to Excessive Temperature:* If the sample is dried at temperatures above 200 F., water from the clay in the sample may be lost in the drying oven. This water is not free or mobile water in the reservoir at bottom-hole conditions. The loss in weight results in an error in the oil content of the core sample.

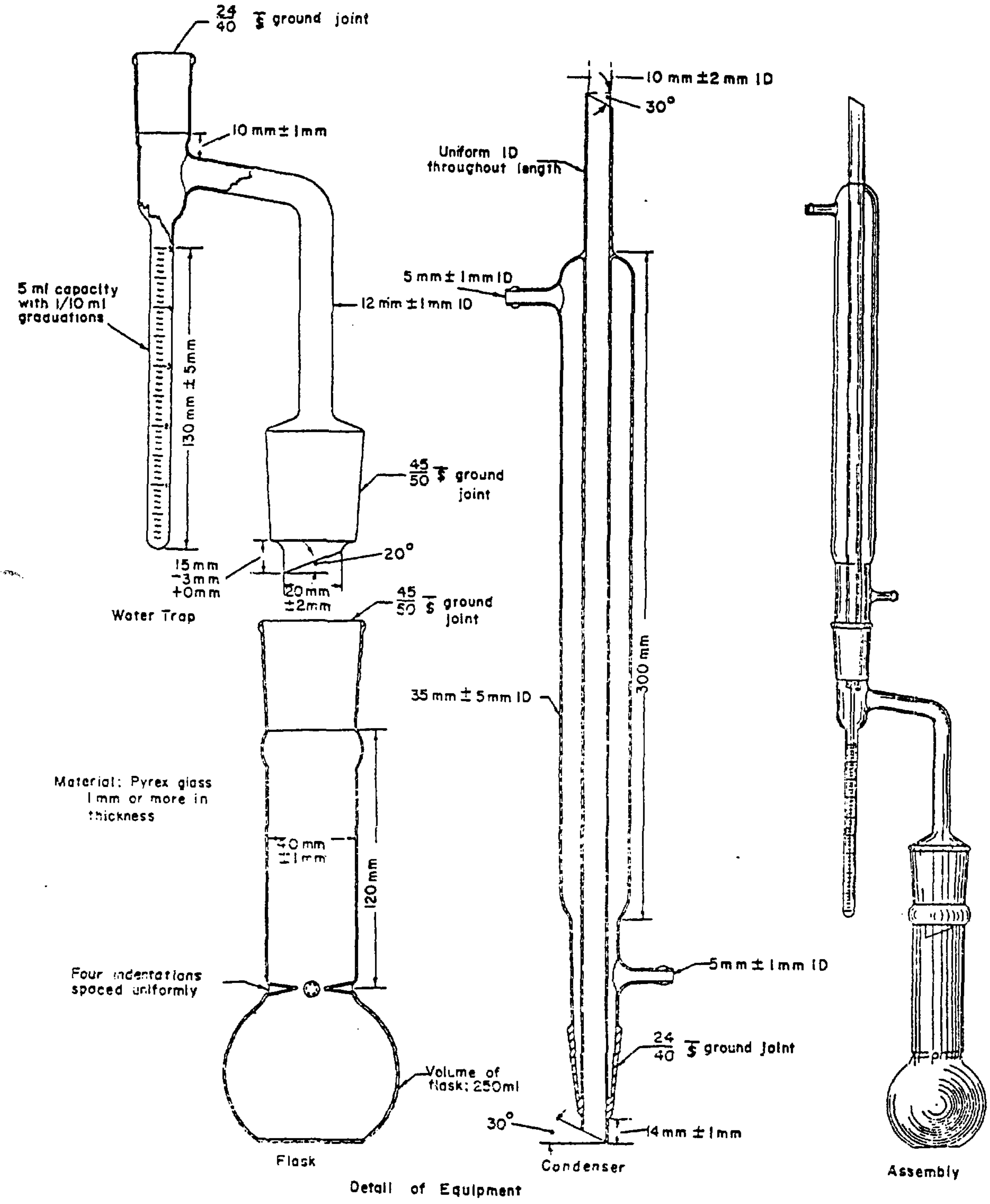


FIG. 3.55F1—APPARATUS FOR SIMULTANEOUS DETERMINATION OF OIL AND WATER SATURATIONS OF OIL SANDS

ɜ error can be minimized by drying at tempera-..res below 200 F. in a vacuum oven.

b. *Incomplete Drying:* If the core sample is not completely dry after extraction, the calculated oil content will be less than the true value. To prevent this error, it is suggested that the samples be dried in a vacuum oven over night when time permits.

3.56 BULK VOLUME BY MERCURY DISPLACEMENT

3.561 Apparatus

a. Steel or glass pycnometer.
b. Container to hold displaced mercury.
c. Balance with accuracy of 0.01 gram.
d. Weighing dish.

3.562 Procedure

The pycnometer is filled with clean mercury and the top is inserted. Excess mercury will be forced through the air hole in the top. The excess mercury is brushed from the top and sides of the pycnometer with a camel's-hair brush. After placing the pycnometer in a suitable container, remove the top, measure the temperature of the mercury, and immerse the sample in the mercury by replacing the top. *(Note:* The inside of the top should be equipped with prongs to force the sample into the liquid. It should also be coned to facilitate removal of trapped air[8]). The sample should not touch the sides of the pycnometer. After the top is seated, brush off any mercury adhering to the outside of top or sides. The mercury displaced by the sample is transferred to the weighing dish and its weight is determined. The bulk volume of the sample is obtained by dividing the weight of mercury displaced by the density of mercury. The density of mercury at the temperature of displacement can be found in chemical or physical handbooks.

Instead of weighing, a direct measure of the bulk volume can be made. The displaced mercury is transferred to a burette or accurately calibrated tube to measure the volume of mercury. This volume is the bulk volume of the sample.

3.57 BULK-VOLUME METER

3.571 Apparatus

Bulk-volume Meter: This instrument measures bulk volume by displacing a suitable liquid into an inclined graduated glass tube by submerging the core sample under mercury in an adjacent connected vessel. The apparatus is shown in Fig. 3.57F1.

3.572 Procedure

The bulk-volume meter is calibrated by submerging a steel blank in the mercury chamber. The mercury volume in the cylinder is adjusted until the oil column reads exactly a definite point on a suitable scale mounted behind the oil column. The meter is previously calibrated with a series of blanks of known volume over the range of interest and a curve drawn for volume vs. scale readings. If room temperature is constant, practically no variation in calibration will be noted after the first 2 or 3 samples have been measured.

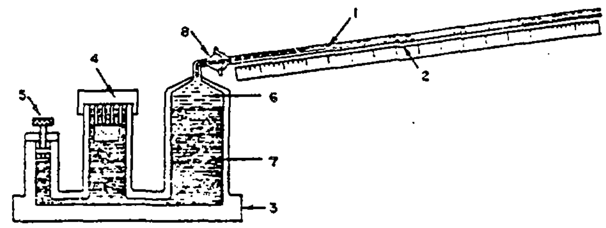
A sample of the core to be examined is submerged in the mercury cylinder and the resultant liquid level is read on the scale. The value read on the scale is converted to volume through use of the calibration curve. The values may be taken from the curve and used in chart form for convenience.

The meter is calibrated every 6 to 10 samples. More frequent calibration is necessary when measuring either friable sandstones (mercury becomes dirty and volume increases), or vugular limestones (vugs trap mercury as sample is removed and mercury volume decreases).

3.58 PORE VOLUME FROM GRAIN DENSITY BY DRY METHOD

3.581 Apparatus

a. Pulverizer with adjustable tolerance between the grinding plates.



1—Precision tubing—bore approximately 3 mm ID.
2—Calibrated scale, reading in cubic centimeters
3—Steel vessel
4—Cap with sample holddown prongs
5—Mercury volume adjustment
6—Oil
7—Mercury
8—Ground joint connection

FIG. 3.57F1—BULK-VOLUME METER

b. U. S. Bureau of Standards, sieves, 60-mesh and 100-mesh.
c. Analytical balance, with accuracy to ±0.1 milligram.
d. Modified Boyle's Law porosimeter.

The porosimeter construction is simple (Fig. 3.58F1), consisting of a board-mounted mercury column with leveling bulb, a 20-ml pipette, an oil manometer, an aluminum cup sample holder, and a connecting mercury-displacement pump with a calibrated milliliter mercury scale having a capacity of approximately 100 ml of mercury.

The column of mercury, pipette, manometer, sample holder, and pump are all connected in sequence with ¼-in. copper and plastic tubing so that pressure exerted into the sample cup from the mercury column registers on the oil manometer and can be counterbalanced by pressure from the mercury-displacement pump. No special materials are necessary. Standard laboratory glassware is satisfactory.

3.582 Procedure

An extracted, dried sample is pulverized and then sieved through a 60-mesh sieve onto a 100-mesh sieve. A 150- to 200-gram portion of the sample remaining on the 100-mesh sieve is placed into a tared 400-ml Griffin beaker and weighed. The weight of the sample is recorded to four decimal places.

Before introduction of the sample, the porosimeter is calibrated to a solid standard of known bulk volume. For the equipment listed, solids having bulk volumes of 40-ml and 50-ml displacement of mercury are used. Either solid is placed into the cup and the cup screwed into place on the apparatus.

With the cup in place, the leveling bulb on the mercury column is raised and/or lowered to fill the 20-ml pipette to a marked-level reference point. This

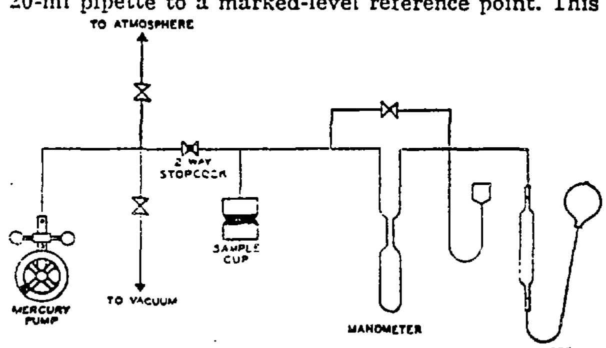


FIG. 3.58F1—SCHEMATIC DIAGRAM OF GRAIN-DENSITY APPARATUS

reference point is permanently etched into the glass of the pipette. The pressure thus exerted into the cup is registered by the oil manometer. The displacement pump, which previously has been brought to rest at zero, is now caused—by slow hand pressure—to counterbalance the mercury column pressure. This is accomplished when the two levels in the oil manometer are equal. Under this condition the milliliters of mercury required are recorded from the calibrated scale of the pump.

This procedure is repeated from beginning to end until at least two final readings on the pump scale are in agreement.

These several readings, as recorded, are averaged; and their mean value is used as the final reading.

The other solid of known bulk volume is also subjected to this procedure.

Once the solid standards have been run, the core sample to be tested is also subjected to this procedure.

There are now three values, viz.:

a. Total volume of empty sample cup.
b. Displacement constant for 1 ml of mercury from pump.
c. Displacement in the cup by the sample.

After several sample runs, it is advisable to recheck the standard solid values. This is necessary because of possible change in the temperature of the instrument which would cause mercury expansion.

3.583 Calculations

The displacement in the cup caused by 1 ml of mercury from the pump is a necessary constant to be applied in calculating the total volume of the empty cup and in calculating total displacement when the cup is occupied by a sample:

$$M = (V50 - V40) / (R40 - R50) \quad (3)$$

Wherein:

M = displacement constant.

V50 = bulk volume of solid (50 ml of mercury displacement in bulk-volume meter).

V40 = bulk volume of solid (40 ml of mercury displacement in bulk-volume meter).

R50 = average of readings obtained from displacement pump, in milliliters, when solid is in sample cup and pressure from mercury column has been counterbalanced by pump.

R40 = average of readings obtained from displacement pump, in milliliters, when solid is in sample cup and pressure from mercury column has been counterbalanced by pump.

Then the total volume of the empty cup is calculated:

$$b = M(R50) + V50 \quad (4)$$

Wherein:

b = total volume of empty cup expressed in milliliters.

M = displacement constant for 1 ml mercury from pump [equation (3)].

R50 = see equation (3).

V50 = see equation (3).

By substituting *R40* and *V40* values in equation (4), the *b's* should equal.

After *M* and *b* are determined, then the grain volume of the sandstone sample is calculated:

$$\text{Grain volume} = b - RM \quad (5)$$

Wherein:

b = see equation (4).

M = see equation (4).

R = averages of readings obtained from displacement pump with sandstone sample in sample cup.

The grain density is then calculated:

$$\text{Grain density} = \text{weight of sample/grain volume} \quad (6)$$

Consequently, the percent total porosity is calculated:

$$\text{Total porosity percent} = \text{bulk volume} - \frac{(\text{weight of extracted, dried saturated sample/grain density})}{\text{bulk volume}} \quad (7)$$

3.59 PORE VOLUME FROM GRAIN DENSITY BY WET METHOD

3.591 Apparatus

a. Mortar and pestle.
b. 100-mesh sieve.
c. 50-cc calibrated volumetric flask and stopper.
d. Constant-temperature water bath.
e. Analytical balance.

3.592 Preparation

Weigh a dry, clean 50-cc volumetric flask and its stopper. Transfer approximately 50 cc of a liquid of known density—e.g., toluene, water, etc.—into the flask. Insert the flask with the liquid into a constant-temperature water bath. Allow the temperature of the liquid to reach equilibrium with its surroundings. To the flask add liquid with an eye dropper until the bottom of the liquid meniscus reaches the 50-cc reference mark.

Remove the flask from the bath and allow to cool. Stopper the flask and weigh the stoppered flask with its contents.

Subtract the weight of the empty stoppered volumetric flask and this result should be the weight of 50 cc of liquid. Record the flask number and the weights for future use.

Crush about 30 grams of the sample in a mortar and sift the powdered sample through a 100-mesh sieve. Continue crushing the coarser particles until grain has been obtained. Transfer the powder and the coarser particles to a petri dish and dry in the oven.

> *NOTE:* Usually a grain density determination is carried out on each successive core sample of the formation if there is a change in the lithology. For a fomation interval of no lithological change, it is recommended that a grain-density determination be carried out on every third successive core sample of the interval.

3.593 Procedure

Using a funnel, transfer about 15 grams of the dried, crushed core sample into a 50-cc calibrated volumetric flask. Weigh the sample in the stoppered flask. The flask containing the sample is weighed to 0.001 gram. The flask and sample are then evacuated for about 20 min. The rate of evacuation at first must be controlled, so that the powdered sample is not drawn into the upper parts of the flask and into the vacuum system. After evacuation, add some liquid to the flask. Whirl the flask and its contents in order to completely wet the powdered sample with the liquid.

NOTE: If water is used as the liquid, a wetting agent should be added to insure complete wetting of the powdered sample.

Add more liquid, almost to the 50-cc reference mark. Insert the flask and its contents into a constant-temperature water bath until the temperature of the liquid in the flask becomes constant. With an eye dropper, add liquid to the flask until the bottom of the meniscus reaches the reference mark. Remove the flask from the water bath and allow to cool. Weigh the stoppered volumetric flask with its contents.

The weight of a 50-cc volumetric flask containing 50 cc of liquid has already been determined in 3.592.

The portion of crushed core sample placed in this flask displaced an equivalent volume of liquid. By determining the density of the liquid and the weight of the displaced liquid, it is possible to calculate the displaced volume of liquid. The weight of the sample has been measured and with the relationship, *grain density = weight of sample volume of sample,* the grain density of the core sample is calculated.

The grain-density value found by experiment is assumed to apply to the whole extraction sample. The grain volume of the extraction sample is given by the quotient of sample weight divided by grain density, and the pore volume is the difference between the bulk volume and grain volume. The total porosity is the quotient of pore volume divided by bulk volume.

3.5.10 BOYLE'S LAW SINGLE-CELL METHOD

3.5.10.1 Apparatus

The Kobe instrument is one example of a Boyle's Law single-cell unit. (Fig. 3.5.10F1). The major piece of apparatus is a piston-type, crank-operated, mercury pump, mounted horizontally. The pump plunger is attached to a precision screw and a micrometer scale. This assembly can be rotated as a unit by a crank. In this way the mercury level in the core chamber can be regulated, and the volume of gas confined can be changed by the operator. Each complete turn of the crank changes the volume of the core chamber 1 cc. The micrometer scale, graduated in 100 divisions, measures differential volumes within the core chamber to 0.01 cc.

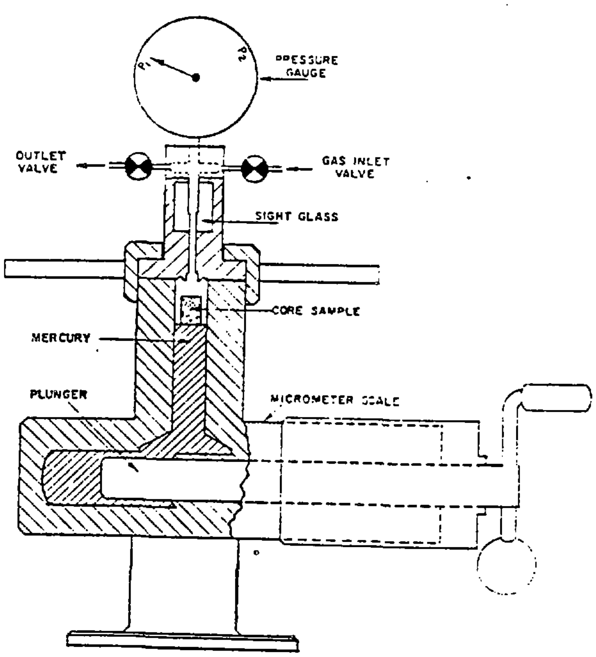


FIG. 3.5.10F1—SCHEMATIC DIAGRAM OF KOBE POROSIMETER

The cylindrical core chamber is mounted vertically on top of the pump. Cores may be introduced into the core chamber through the top, and float on the mercury inside. A removable threaded cap seals the core chamber. A sight glass with a reference line is situated at the top of the cap. This glass is a part of the core chamber and is concentric to it. Above the sight glass, there are two openings to the core chamber—the first, the inlet valve to admit gas (usually air or helium); and the second, the outlet valve which is a vent to the atmosphere.

A precision pressure gage is attached at the top of the closure assembly to register pressure within the core chamber. Only two pressures need be indicated by this gage: *a*, Atmospheric pressure, or P_1; and *b*, an elevated pressure, P_2. The latter pressure level, P_2, is on the order of three to four atmospheres absolute. The gage used must be capable of indicating these two pressure levels precisely. The earlier instruments used a dead-weight gage. Some of the later models use a Bourdon-type gage. On some instruments, the gage is mounted to one side of the porosimeter and connected to the top of the core chamber by a small-bore metal tube in order to reduce the weight of the cap assembly. There should be some degree of flexibility in the tube to enable the operator to open and close the core chamber. Instruments equipped with a dead-weight gage should have a means of ascertaining whether the gage piston has been raised to a reference level. This can be done easily by projecting a magnified image of an indicator (attached to the gage) onto a screen with a reference line drawn across it.

Even though a number of refinements have been made by some users, the basic principles and operating procedures remain about the same. The following procedure is a description of the operation of the Kobe unit.

3.5.10.2 Procedure

a. Close and seal core chamber.

b. Be sure gas inlet valve is closed.

c. Outlet valve should be open.

d. By means of the pump, raise the mercury level in the core chamber to the reference line on the sight glass. The stroke described is a *displacement* stroke. To minimize errors from backlash, the pump should be advanced in approaching a reference point or compression reading. Under these conditions, the operator would be turning the crank clockwise on approaching a point where a reading is to be made.

e. Note and record the micrometer reading at this point. This reading will be called R_1.

f. Open the gas inlet valve. Gas should be admitted to the core chamber so that only a small amount bleeds from the outlet valve (wide open) during step g.

g. Retract the pump to about 2 cc beyond the starting point. Use of only one starting point is advised wherever possible. Some users find the 50-cc level usable for most cores. Larger samples may require that the 75-cc starting point be used.

h. Close gas inlet valve.

i. Advance pump plunger to starting point.

j. After pausing momentarily, close the outlet valve. At this point, the gas confined in the core chamber is at P_1, or atmospheric pressure. Volume of gas in the chamber at this point is V_1 at P_1.

k. Advance the pump plunger until gas in the core chamber is compressed to P_2.

l. Read the value indicated on the micrometer scale. This reading is R_2 and the pressure is P_2. Volume of gas is V_2.

One displacement and one compression stroke have been described. Since no sample was in the core chamber, this pair of readings is called a "blank run" or "blank."

m. Open the outlet valve slowly to bring the pressure in the core chamber to atmospheric (P_1). On models using the dead-weight gage indicator, the pump plunger should be retracted a few turns to lower the piston in the gage to the point of rest, prior to opening the outlet valve. This is to prevent the gage from dropping back sharply upon releasing the pressure.

n. After the blank run has been completed, open the core chamber and insert a sample.

o. With the sample in the core chamber, follow the procedure outlined in steps a. through m.

p. The micrometer value for the displacement reading will be termed R_3.

q. The value for the compression reading will be called R_4, and the pressure will again be P_2. The volume of gas at P_2 will be V_4 (at the start of the compression stroke, it was V_3 pressure P_1).

r. Remove core. Leave instrument with gas inlet valve closed, outlet valve open.

3.5.10.3 Determination of Compression Factor C_f

a. Make a "blank run" (in this case, displacement reading is not needed) using the customary starting point L_o. The compression reading so obtained is C_o.

b. Complete a second blank run in a similar manner as step a., *EXCEPT* use a lower starting point, $L_o—10$. For example, if 50 is the usual starting point, it is suggested that the blank run in step a. should start at 50 and in step b. at 40. This will give the effect of placing a 10-cc non-porous solid in the core chamber of the porosimeter.

c. The compression factor can be computed from the formula:

$$C_f = 10/[10 - (C_o - C_1)] \quad (8)$$

d. It should be emphasized that appreciable barometric pressure changes affect the compression factor considerably and that, in localities where significant changes occur, this factor should be computed and charts made to cover the ambient barometric range. The compression factor can also be expressed by the relationship:

$$C_f = P_2/(P_2 - P_1) \quad (9)$$

Wherein: P_2 is the floating pressure, and P_1 is barometric pressure.

e. The micrometer scale calibrations can be checked by adding a weighed amount of mercury to the instrument and noting the resulting shift in the displacement readings.

3.5.10.4 Calculations

The four readings which have been made are:

	Displacement Stroke	Compression Stroke (P_1 to P_2)	Volume Reduction At P_1 At P_2
Blank run	R_1	R_2	V_1 to V_2
Sample run	R_3	R_4	V_3 to V_4

From these data bulk volume, grain volume, and pore volume can be calculated in the following manner:

a. Bulk volume $= R_3 - R_1$.

b. Grain volume $= C_f (R_4 - R_2)$. C_f = compression factor.

c. Pore volume = (bulk volume — grain volume) $= (R_3 - R_1) - C_f(R_4 - R_2)$.

Operators have noted that the first one or two sample runs in this type of porosimeter are erratic. This is caused by the Joule-Thompson effect. For best results, prior to running a group of samples the operator should make two or three blank compression runs. It is recommended that the instrument be operated at the rate of about 20 to 30 samples per hour.

The gas inlet should be connected to a supply of dry gas to prevent condensation of water during the compression strokes. If air is used, it should pass through an adequate drying tube prior to entering the inlet valve. The use of helium has produced the most satisfactory results, since it is adsorbed on surfaces only very slightly whereas the dimolecular gases such as nitrogen and oxygen are very noticeably adsorbed. When using helium, it is superfluous to evacuate the core in the core chamber to remove air prior to beginning a compression stroke. If helium is used, and the sample chamber is flushed with helium but not evacuated, virtually all the air remaining within the core chamber is within the pore channels of the sample. During the compression stroke, the partial pressure of the air inside of the core, and hence the degree of adsorption, remains unchanged.

3.5.10.5 Precautions

The sensitivity of this type porosimeter during compression strokes can be impaired if the gas volume around and above the core is excessively large in comparison to the core volume being measured. For this reason, it is imperative to make all gas passages above the core chamber to the gage and the valves as small and as short as practical. In this regard, it is also advantageous to begin a compression run at the lowest practical starting point. Cores should still float on top of the mercury at the end of each compression stroke. If cores are deeply immersed in mercury during this operation, passages to some pores are obstructed to the flow of gas, and in some cases the core can even be caused to imbibe mercury.

3.5.11 BOYLE'S LAW—DOUBLE-CELL METHOD

3.5.11.1 Procedure

Basically, the instrument consists of two connected chambers with a means of measuring the pressure in each chamber. Following a bulk-volume measurement, the core sample is placed in one chamber and the gas pressure in this chamber is adjusted to some known value. The gas in the second chamber is adjusted to some different known pressure. The pressure is equalized and measured and the final volume is known.

From these data and Boyle's Law, the grain volume is calculated.

Three distinct modifications of the procedure are in general use, as discussed following.

Modification A[9]

In this modification, the pressure in the core chamber is initially atmospheric, while that in the second chamber is some fixed higher value in the range of 40-100 psig. The pressure is equalized between the chambers and measured. To simplify calculations and to compensate for slight deviations from Boyle's Law, the instrument is calibrated with known volumes in the core chamber, and the relationship between grain volume and the final pressure is developed empirically. Sample grain volumes are then read from the prepared table of volumes vs. pressure readings.

Modification B

This modification is similar to modification A, except that the pressure in the core chamber is initially a fixed high value (about 10 psig) while the other chamber is at atmospheric pressure. The apparatus is shown in Fig. 3.5.11F1.

Let: V_z = grain volume, in cc.
V_o = volume of cell, in cc.
P_o = high-pressure manometer reading, in cm.
P_a = atmospheric pressure, in cm Hg.
V_L = volume of lines from cell valve to mercury surface of reading manometer, in cc.
C = cross-sectional area of reading manometer, in sq cm.
R = reading of manometer, in cm.
K = instrument constant zero pressure reading.

Then: $V_z = V_o - [V_L + C\ (P_a + K - R)]\ /(P_o/K - R) - 1$ (10)

assuming that the ideal gas law applies for helium at the pressures used.

Modification C[10]

As in modification B, the core chamber is initially at high pressure, but the gas is then expanded into a gas burette where the volume at atmospheric pressure is measured.

Let: V_B = volume of the bomb.
V_g = volume of gas in the burette.
P_B = absolute pressure of gas in the bomb.
P_g = absolute pressure of the gas in the burette (also the pressure of the gas in the bomb after expansion of gas).
y = the factor to compensate for the deviation of a gas from the ideal gas law at pressure P_g.
V_X = grain volume.
$V_B = V_g/[(yP_B/P_g) - 1]$

NOTE: Equation (6) of ref. 10 is in error. This formula is likewise applicable in determining the void space in the bomb with the specimen in it (V_Y).

Then: $V_z = V_B - V_Y$ (11)

Effective porosity is then reported as percent of bulk volume.

The greatest sensitivity is obtained from the porosimeter when the core sample is as large a portion of the core-chamber volume as is possible. Most users of the Boyle's Law type porosimeters have found it advisable to set up a definite time cycle in the operation of the instrument. The same timing is followed both in calibration and in porosity determinations. In this way, the changes in the temperature of the gas

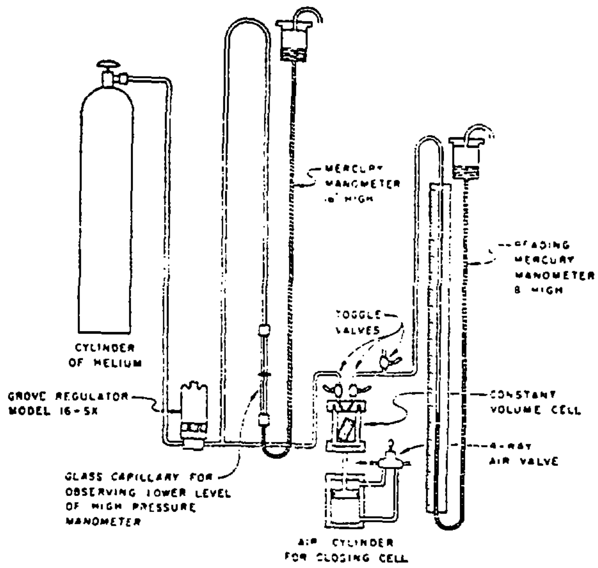


FIG. 3.5.11F1—BOYLE'S LAW DOUBLE-CELL *POROSIMETER*

caused by expansion and compression are accounted for in the calibration. The accuracy for small cores can be increased by using a smaller core chamber or by partially filling the chamber with solids of known volume.

3.5.12 WASHBURN-BUNTING METHOD[6]

3.5.12.1 Procedure

The rock specimen is placed in a sample chamber as shown in Fig. 3.5.12F1, and the following steps are performed.

a. Make a blank determination with a piece of glass of approximately the same shape and size as the core sample to be tested. This gives a zero reading which corresponds to adsorbed air on the surface of the test piece.

b. Place the core sample in the sample chamber above the mercury and leave the upper stopcock open.

c. Raise the leveling bulb until the mercury reaches above the stopcock. This must be done slowly and carefully in order to avoid the jetting of mercury through the upper stopcock.

d. Close the stopcock.

e. Lower the leveling bulb until the core floats in the barometric vacuum on top of the mercury. Let the core stand in this position for a few minutes in order to allow the complete escape of air from the core.

f. Lift the leveling bulb slowly until the two levels in the two branches are at the same height. This assures the restoration of atmospheric pressure on the air which escaped from the core. Steps e. and f. should be repeated a minimum of 3 times. Since the apparatus as well as the core is presumably at room temperature, the air volume in the graduated capillary represents the true effective pore volume of the core.

The effective porosity in percent is given by:

$\phi = 100$ [*(Volume from step f.—zero reading from step a.)/bulk volume*] (12)

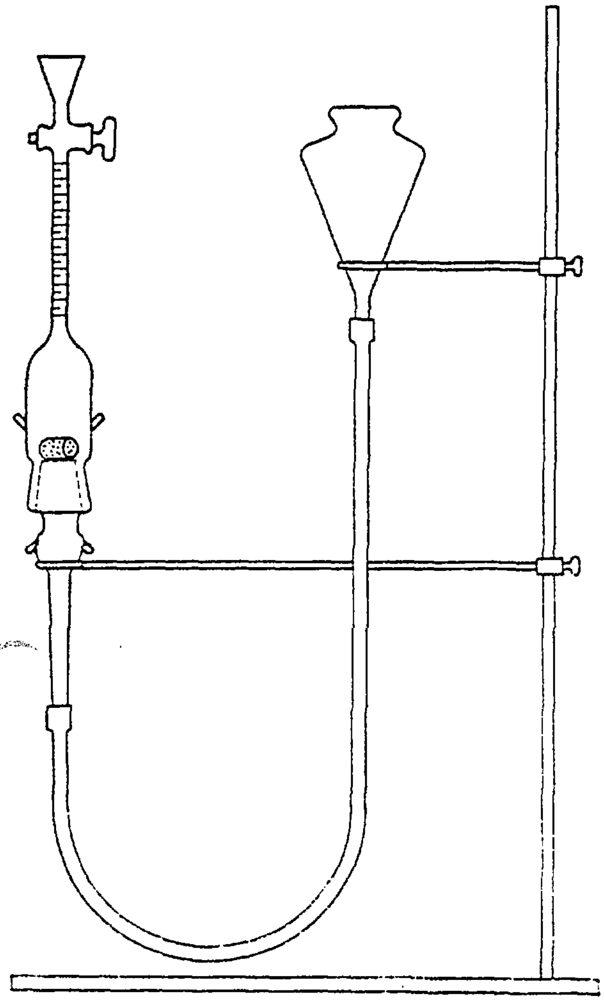


FIG. 3.5.12F1 — WASHBURN-BUNTING TYPE POROSIMETER

3.5.13 HYDROCARBON RESATURATION METHOD

3.5.13.1 Apparatus

a. An analytical balance accurate to 1 milligram, preferably one on which rapid weight determinations can be made.

b. A suitable vacuum source capable of maintaining 0.01 mm of mercury pressure.

c. Suitable containers which can be used to hold cores and deaerated liquid under vacuum.

d. A filtered low-viscosity, low-vapor-pressure liquid of known density for the purpose of saturating the core samples. (Some liquids which have been used are kerosene, white oil, toluene, and decane.)

3.5.13.2 Procedure

a. Obtain the weight of the dry, clean sample. (The sample should be desiccated over a suitable dehydrating material, such as $CaCl_2$, prior to the determination of the dry weight. The desiccating period should be long enough to eliminate water vapor from the dry sample.)

b. Place the weighed, dry sample in a chamber (vacuum flash or dessicator) and apply a high vacuum for about 8 hours. For very low-permeability samples, the evacuation period should be as long as 12 to 18 hours (overnight).

c. At the end of the evacuation period, a deaerated liquid is drawn slowly into the evacuated vessel containing the core sample. The core is allowed to saturate by capillary action. After the sample has been completely submerged in the liquid, the vacuum is continued for an additional 30 min to 1 hour, or until all evidence of bubbling has ceased.

d. The evacuated chamber containing the core completely submerged is then opened to the atmosphere for at least 1 hour; then the vacuum is applied again for a period of at least 1 hour. This is necessary to assure as complete saturation of the sample as possible. After the vessel has again been opened to the atmosphere for 30 min to 1 hour, the sample is ready to be weighed. (Some laboratories prefer to soak the samples for 24 hours under a good vacuum and others include a step pressuring the liquid surrounding the sample to as high as 3,000 psi to assure complete saturation.)

e. The sample is removed from the saturating vessel and weighed submerged in the saturating liquid, utilizing a suitable arrangement on the analytical balance which will allow the sample to be suspended freely in the liquid. (The tare weight of the suspended device must be determined prior to weighing the sample.)

To facilitate weighing the samples, an automatic balance may be altered by removing the pan and replacing it by a counterweight and sample cradle such that the cradle, when suspended in the liquid, will have an apparent weight of zero. Care should be taken that, at the surface of the liquid, only the fine suspending wire passes from the air into the liquid. An error would occur if a portion of the cradle or the sample disturbed the surface of the liquid.

The saturated samples are placed in a tray of sufficient depth for complete submersion of the samples and cradle in the liquid and sufficient breadth to allow manipulation of the samples by tongs while the tray is within the balance. If transfer of samples through air is necessary, it should be done rapidly to prevent evaporation from the pores. By using a smaller container for saturation in the vacuum desiccator and placing this into the larger tray of liquid, a transfer in air is unnecessary.

Each sample is individually weighed on the cradle while suspended under the liquid. As each weighing is completed, the weighed sample should be returned to another position in the tray, and not removed from the tray. This is important since the level of the liquid must be kept constant in order to obtain good accuracy. After weighing each batch of samples, density of the liquid is determined. This must be done with accuracy, since on permeable samples at least, the liquid density is probably the greatest source of error. A good-quality pycnometer should be used. Weighings should be performed rapidly and the liquid density taken immediately so that temperature corrections are minimized. Temperature of the liquid should not vary by more than 1 deg F. during the measurements on one group of samples.

f. The saturated weight of the sample is determined after carefully hand-blotting the excess surface liquid from the sample. Blotting materials such as cloth or paper may desaturate the sample. Therefore, hand wiping is preferred. (If the pore volume of the sample is already known from another measurement, this step may be omitted.)

3.5.13.3 Precaution

Error can be introduced into this procedure for the determination of pore volume and bulk volume by: *a*, not attaining 100-percent liquid saturation of the core sample during the evacuation procedure; and *b*, improper surface wiping of the sample prior to the determination of the saturated weight.

3.5.13.4 Calculations

The procedure for the calculation of effective porosity is outlined following.

a. Net submerged weight = submerged weight — tare weight of the device used to suspend the sample in the liquid media.
b. Weight of liquid in the sample = saturated weight—dry weight.
c. Pore volume = weight of liquid in the sample ÷ liquid density.
d. Bulk-volume buoyancy = saturated weight — net submerged weight.
e. Bulk volume = bulk-volume buoyancy ÷ liquid density.
f. Grain-volume buoyancy = dry weight — net submerged weight.
g. Grain volume = grain-volume buoyancy ÷ liquid density.
h. Pore volume = bulk volume — grain volume. (Any difference between this pore volume and the pore volume in c. indicates an arithmetic error.)
i. Effective porosity = pore volume ÷ bulk volume.
j. Grain density = dry weight ÷ grain volume.

3.5.14 MERCURY-PUMP METHOD
(U. S. Patent No. 2,874,565)

3.5.14.1 Apparatus

The mercury pump, Fig. 3.5.14F1, is a high-pressure volumetric displacement pump to which a high-pressure stainless-steel sample chamber is attached. The displacement is accomplished by a screw-actuated plunger which operates through a packing gland into a cylinder. The plunger and a micrometer scale attached to its actuating screw are precisely machined, allowing the displacement of the plunger to be read very accurately, the micrometer scale being graduated in units of 0.01 cc. A linear scale past which the plunger moves is graduated in cubic centimeters. The sample chamber, which will hold samples up to approximately 25 cc, is closed by a cap equipped with a needle valve which allows the chamber to be purged of air. The cap seats against an O-ring and is locked in place by a quick-action yoke-and-screw device. The cap is fitted with small stainless-steel pins to prevent the sample touching the top or sides of the chamber. A vacuum gage is connected to the cylinder to indicate the pressure of the system. A high-pressure valve is placed between the cylinder and the vacuum gage to protect the vacuum gage when the system is under pressure. The mercury in the system is continuous from the cylinder to the gages and into the bottom of the sample chamber, so that when a sample is in the chamber and the chamber is filled with mercury, there is no gas in the entire system except that which may be in the pore space of the sample or purposely introduced for calibration purposes.

3.5.14.2 Procedure

The bulk volume of a cleaned and dried core sample of 10 to 20 cc in volume, either shaped or irregular, is obtained by mercury displacement. The pressure in the vessel containing the sample and the confirming mercury is reduced to approximately half an atmosphere. The volume of the expanded air or gas from the core space is measured accurately. The pore volume is calculated using Boyle's Law. The percent porosity is obtained from the pore volume and bulk volume measurements. The procedural details follow.

a. Place cap on sample chamber, lock it in place and open the needle valve.

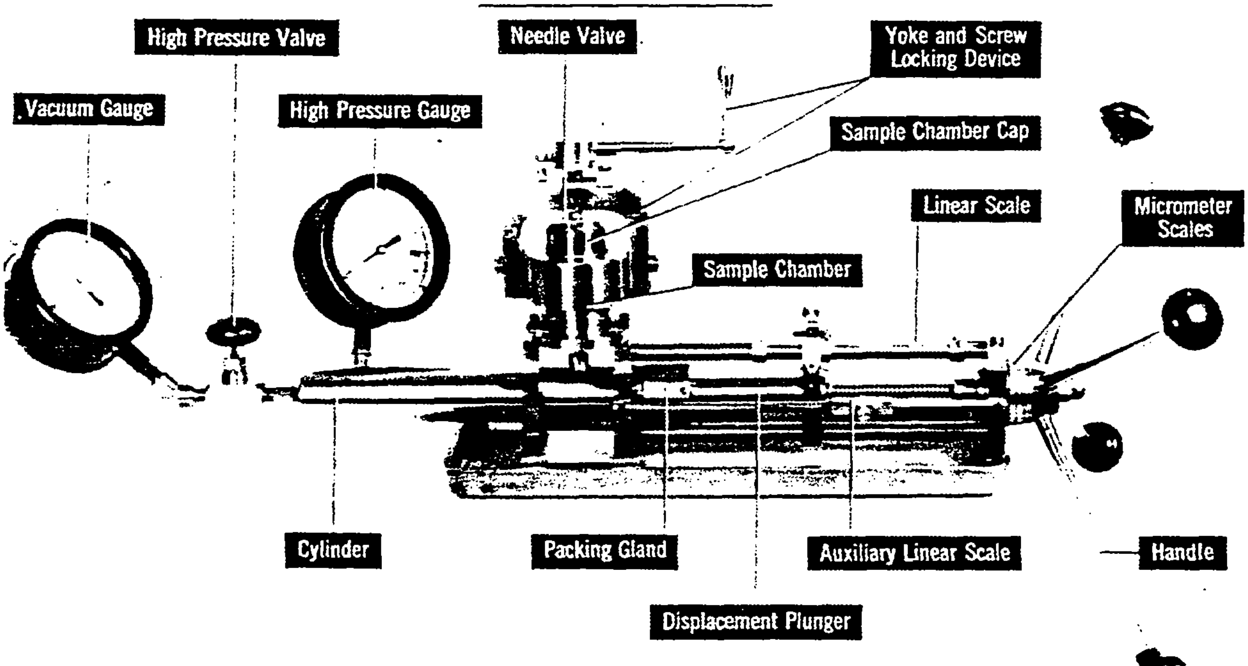


FIG. 3.5.14F1—MERCURY PUMP

b. Open the high-pressure valve to the vacuum gage three quarters of a turn.

c. Displace the pump plunger so as to advance the plunger into the cylinder until the sample chamber is completely filled with mercury, i.e., until a small drop of mercury appears in the recess below the needle valve. The amount of mercury in the recess should be such that no mercury shows above the needle valve when it is closed, and no air should be trapped below the needle valve when it is closed.

d. Set the vacuum-gage pointer to zero.

e. Set the pump scales to zero.

f. Close the needle valve firmly, so it will not leak subsequently when vacuum is applied.

g. Withdraw the pump plunger until the vacuum gage reads 16 in., tapping the gage during this time to insure free movement of the pointer.*

h. Record the micrometer scale reading and label it *C*.

i. Open the needle valve and withdraw the plunger to between 5 and 6 cc. Return the pump to exactly 5.00 (use both linear and micrometer scales).*

j. Close the needle valve.

k. Withdraw the plunger until the vacuum gage reads 16 in., tapping the gage as before.*

l. Record the linear-scale and the micrometer-scale readings as one reading and label it *R*.

m. Open the needle valve and advance the plunger into the cylinder until the scales read 5.00, as in step i.

n. Repeat steps j. through m. until five *R* values have been recorded. Obtain an average of five *R* values.

o. Calculate a factor, *f*, using the following formula:

$$f = 5.00 \,/\, [R\ (avg.) - C - 5.00] \qquad (13)$$

p. Open the needle valve and repeat step c. to rezero the pump.

q. Withdraw the plunger approximately 30 cc.

r. Open the sample chamber and insert a sample that has been extracted and dried. Replace and lock the cap.

s. Advance the plunger into the cylinder carefully until a drop of mercury appears in the recess below the needle valve as in step c.

t. Record the linear-scale and micrometer-scale readings as one reading. This is the bulk volume of the sample in cubic centimeters.

u. Set the linear scale to zero and the micrometer scale to the value of *C* found in step h.

v. Close the needle valve.

w. Withdraw the plunger until the vacuum gage reads 16 in. as in step g.

x. Record the linear-scale and micrometer-scale readings as one reading. This is the apparent pore volume of the sample.

y. Multiply the apparent pore volume found in step x. by the factor, *f*, found in step o. The product is the true pore volume.

z. Divide the true pore volume found in step y. by the bulk volume found in step t. and multiply the quotient by 100 to obtain the percentage by volume of pore space.

***To minimize errors caused by backlash, all pump readings should be taken as the plunger is being advanced into the cylinder, except for the vacuum readings. The vacuum readings should be taken as the plunger is withdrawn from the cylinder.**

A study of the foregoing procedure will show that the gas (air) in the pore space of a sample is expanded to approximately twice its original volume because the pressure of the system is reduced to approximately half of the barometric pressure. Since there is no air in the system other than that which may be in the sample pores, it follows that the amount of displacement of the pump plunger necessary to reduce the pressure to 16 in. of vacuum is an approximate measure of the pore volume. The calibration factor *f* converts the approximate, or apparent, pore volume to the correct pore volume.

In practice, it is impractical for several reasons to use exactly half of the barometric pressure as a reference vacuum pressure. Therefore, a vacuum reference of 16 in. is used, regardless of the barometric pressure, and the instrument is calibrated to measure pore volume empirically. The calibration factor compensates for the pressure ratio, the single-arm manometer effect of the vacuum gage, and the head of mercury on the sample after the expansion has been effected. The pump correction found in step h. corrects for vacuum gage displacement and small amounts of air that may be trapped in the system.

Steps c. through o. constitute the calibration procedure and need not be repeated for each sample. A calibration should be made when starting a set of samples, and occasionally thereafter.

3.5.15 AIR PERMEABILITY DETERMINATION

3.5.15.1 Procedure and Calculations

The dimensions of the core sample must be obtained to calculate its permeability. The length and cross-sectional dimensions may be measured directly by calipering or from measuring the length and computing the cross-sectional area by dividing the bulk volume by the length. These measurements are made before the sample is measured for permeability. If the sample is to be mounted in plastic or pitch, it must be measured before mounting. However, if a mounted core is cut or sectioned to clean the ends, the length must be remeasured after the cutting.

The clean sample is placed in an appropriate holder in the permeameter so that any bypassing of air around the sides of the sample or the mounting is eliminated. Dry air is passed through the core and the rate of flow of the air determined from the pressure difference across a calibrated orifice or other suitable flow-rate measuring device. The differential pressure across the sample may be adjusted to give appropriate or convenient rates of air flow. The inlet air pressure and the air flow rates are recorded. From these measurements and the sample dimensions, the permeability may be calculated. The dry-air permeability may be calculated by the following formula:[11]

$$k = [(2{,}000\ Q_o\ p_o\ L\ \mu) \,/\, (p_i^2 - p_o^2)A] \qquad (14)$$

Wherein:

k = permeability to dry air, in millidarcys.

Q_o = rate of flow, in cubic centimeters per second, of outlet air.

p_o = outlet pressure, in atmospheres (absolute).

p_i = inlet pressure, in atmospheres (absolute).

μ = viscosity of air, in centipoises (see Table 3.5.15T1).

L = length of sample, in centimeters

A = cross-sectional area perpendicular to direction of flow, in square centimeters.

TABLE 3.5.15T1
VISCOSITY OF AIR AT ONE ATMOSPHERE
Viscosity,* μ, in micropoises
(1 micropoise = 10^{-6} poise)

A: Temp., Deg F.	30	40	50	60	70	80	90	100
0	......	174.0	176.8	179.6	182.4	185.0	187.7	190.4
1	......	174.3	177.0	179.9	182.6	185.3	188.0	190.7
2	171.8	174.6	177.3	180.1	182.9	185.6	188.3	190.9
3	172.1	174.9	177.6	180.4	183.2	185.9	188.5	191.2
4	172.4	175.1	177.9	180.7	183.4	186.1	188.8	191.4
5	172.7	175.4	178.2	181.0	183.7	186.4	189.1	191.7
6	172.9	175.7	178.5	181.2	183.9	186.6	189.3	192.0
7	173.2	176.0	178.7	181.5	184.2	186.9	189.6	192.3
8	173.5	176.2	179.0	181.8	184.5	187.2	189.8	192.6
9	173.7	176.5	179.5	182.1	184.8	187.4	190.1	192.8
								193.1

B: Temp., Deg C.	0	10	20	30	40
0	171.8	176.8	181.8	186.6	191.4
1	172.3	177.3	182.3	187.1	191.9
2	172.8	177.8	182.8	187.6	192.4
3	173.3	178.3	183.25	188.1	192.9
4	173.8	178.8	183.7	188.6	193.3
5	174.3	179.3	184.2	189.1	193.8
6	174.8	179.8	184.7	189.5	194.3
7	175.3	180.3	185.2	190.0	194.7
8	175.8	180.8	185.7	190.5	195.2
9	176.3	181.3	186.2	191.0	195.7

*Calculated from Sutherland's equation:

$$\frac{\mu}{\mu_o} = \left[\frac{T_o + C}{T + C}\right]\left[\frac{T}{T_o}\right]^{3/2}$$

Wherein: the temperatures are measured above absolute zero (—273 C.), and C is taken as 120 deg for air.† The standard viscosity is μ_o = 183.25 micropoises at T_o = 23 C. = 296 K., based upon independent observations by six investigators, evaluated by Birge.‡

†Montgomery, R. B: *J. Meteorology*, **4**, 198 (1947).
‡Birge, Raymond T: *Am. J. Phys.*, **13**, 63 (1945).

Calculations may be simplified by any one of several methods. One method is to use specific inlet pressures and such a low pressure drop across the rate-measuring orifice that the outlet pressure is essentially one atmosphere.

The formula then reduces to the following:

$$k = QFL/A \tag{15}$$

Wherein:

$$F = \frac{2000\ \mu\ p_o}{(p_i^2 - p_o^2)} = \frac{2000\ \mu}{(p_i^2 - 1)}$$ (a constant for each fixed inlet pressure, where p_o = 1 atmosphere)

The viscosity, μ, is the viscosity of air under the conditions used to calibrate the orifice. The permeameter compares the pressure differences across the core and the orifice. Since the same air flows through both, any change in air viscosity from either temperature changes or water vapor will have no effect on the relative pressure readings.

A second method of simplifying calculations involves preparing calibration charts or tables showing the permeance* vs. the outlet pressure for given inlet pressures and orifices. The following formula applies:

$$k_c = \frac{L_c}{A_c}\left(\frac{k_{or}}{L_{or}/A_{or}} \cdot \frac{\Delta p_{or} Q_c}{\Delta p_c Q_{or}}\right) \tag{16}$$

Wherein:

k_c, k_{or} = permeability of the core and the equivalent permeability of the orifice, respectively, millidarcys.

Δp_c, Δp_{or} = pressure drop across the core and orifice, respectively, atmospheres.

Q_c, Q_{or} = flow rate through the core and orifice, respectively, cubic centimeters per second.

*The permeance, usually referred to as "apparent permeability," is the proper term for flow capacity. Its use is analogous to the term "conductance" for the flow of current through an electrolyte solution. Permeance bears the same relationship to permeability as conductance to conductivity.

L_c, L_{or} = length of the core and orifice, respectively, centimeters.

A_c, A_{or} = cross-sectional area of the core and orifice, respectively, square centimeters.

This equation can be reduced to:

$$k_c = \frac{L_c}{A_c} \cdot \frac{Q_c}{\Delta p_c} \cdot \textit{orifice constant} \qquad (17)$$

A standard permeable plug can be used to determine the orifice constant directly. If one prepares tables or nomographs from measured outlet pressures, p_o, for given inlet pressures and orifices, then the equation can be reduced further to:

$$k_c = \frac{L_c}{A_c} K^{\theta}_{c} \qquad (18)$$

Wherein: K^{θ}_{c} is the permeance of the core.

The permeance, obtained as described above, is multiplied by the L/A ratio, or L^2/*bulk volume* ratio of the core to give the permeability k_c.

Further simplifications may be made by the use of nomographs, calibration charts, or tables. The value of μ may be fixed for an average room-temperature condition and p_o may be made equal to one atmosphere.

3.5.15.2 Apparatus

a. Pressure Measurement

The pressure drop across the core sample is measured as shown in Fig. 3.5.15F1. A fixed pressure of air between 1 and 80 cm of mercury is supplied g a suitable pressure regulator. Mercury, oil, or

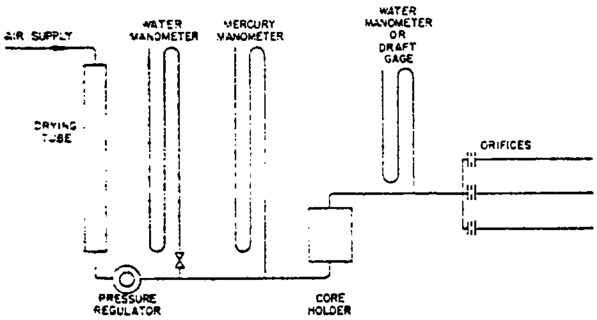


FIG. 3.5.15F1—AIR PERMEAMETER

water manometers may be used to obtain the desired accuracy on the core inlet and outlet pressures. Bourdon-type gages are not reliable and should not be used when attempting to obtain reproducible measurements.

b. Flow-rate Metering Devices

The flow-rate metering devices used are of three types:

1. Calibrated orifices. (A capillary tube which is calibrated for the conditions of testing, so that the pressure drop across the orifice is small compared to the core.)
2. Soap bubble in a calibrated burette.
3. Water-displacement meters.

c. Core Mounting and Holders

Two main types of core holders are used for conventional samples:

1. The Hassler-type (holds cylindrical samples or cores mounted in cylindrical castings or rings), Fig. 3.5.15F2.
2. The Fancher-type (for cylindrical and rectangular samples), Fig. 3.5.15F3.

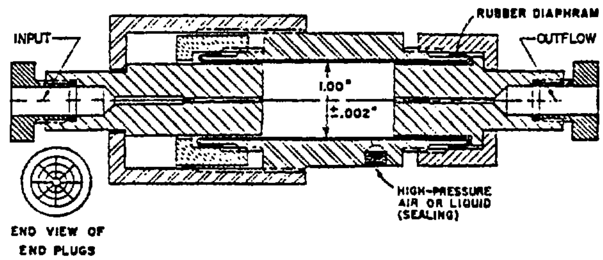


FIG. 3.5.15F2—HASSLER-TYPE PERMEABILITY CELL

The Hassler sleeve-type holder shown in Fig. 3.5.15F2 may be used with cores which are not mounted but are reasonably cylindrical and uniform in cross section, or with cores which have been mounted in potting plastic or supported by pitch in metal or pyrex rings. The sleeve material must be pliable enough to allow complete sealing around the core sample. To accomplish this, a minimum of 100 psi differential between the outside sleeve pressure and the pressure at the inflow face of the sample should be used. For routine-analysis standard practice, using either the Hassler- or the Fancher-type core holder, it is necessary to be certain that the sample is sufficiently strong to prevent deformation by the pressures exerted with the holder. In tests using soft sandstones with a Fancher core holder, it was found that the permeability value depended upon the operator. An

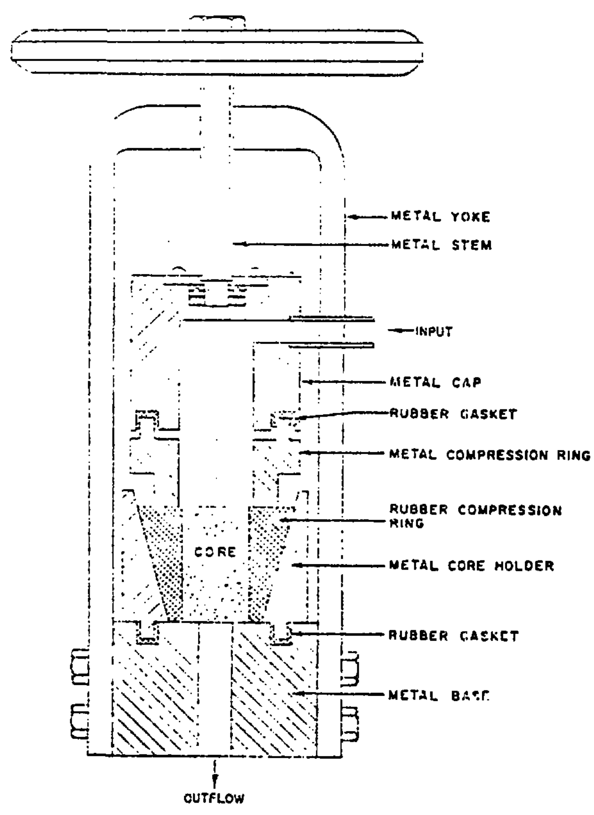


FIG. 3.5.15F3—FANCHER-TYPE CORE HOLDER

appreciable change in permeability was effected, depending upon how tightly the rubber was forced against the core. When such cores were mounted in plastic, metal, or glass rings, and the core surface was effectively sealed, all operators obtained the same permeability values.

If the cores are sufficiently hard and consolidated, they may be run in either the Hassler sleeve or the Fancher holder without support provided by any mounting medium. However, friable, soft, or shaly cores may require mounting. Either optical pitch or a suitable potting plastic may be used for this purpose. The pitch is used to seal the sample in either a metal or pyrex glass ring. The potting plastic may be used to replace the pitch or may be cast around the sample to form a sylindrical mount (see Appendix 3.5.15A1). In any case where a sample is potted or mounted, the Hassler sleeve and the mounting must be such as to insure that the sides of the sample are completely sealed. A compression holder (Fig. 3.5.15F4) may be used instead of the conventional Hassler sleeve for samples mounted in rings. The ends of the core must be clean and open to air flow, and the core must be sealed on the sides to the mounting medium. The permeability measurement is extremely sensitive to the slightest crack. If a crack is suspected, it may be checked by pouring a film of acetone on the surface of the core while the air is passing through it. A row of bubbles may indicate a crack.

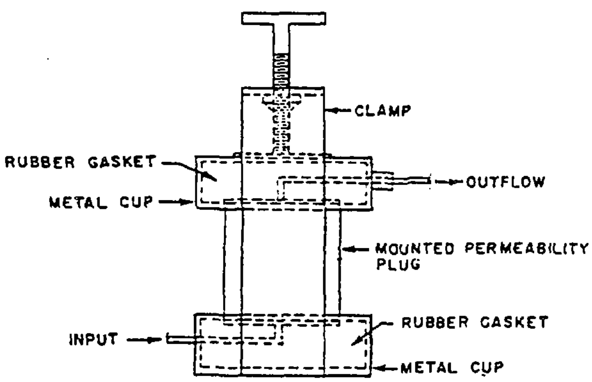


FIG. 3.5.15F4—COMPRESSION CELL FOR RING-MOUNTED CORE SAMPLES

3.5.15.3 Precautions

a. The permeameter shall be checked regularly by means of capillary tubes with various known permeabilities or with standard plugs.

b. Check all cores for cracks or fractures, particularly if high results are obtained. If there are any cracks, samples should be rejected. Mounted samples may be tested for leaks by pressing one face of the ring against a holed rubber stopper fastened to the air supply. Air is passed through the core and, by means of soap and water or acetone, it may be ascertained if the air is issuing uniformly through the end of the core or through a crack. If the air issued uniformly, the air permeability as read was probably correct. If the air issued at one point or crack in the core or between the mounting medium and the core, the result was not satisfactory. If the seal was poor, an attempt should be made to reseal and retest before rejection of the sample. The sample must be thoroughly redried before retesting.

c. The sample holder of the permeameter must be such that when pressure is applied at one end of the system, all flow is through the sample. Care must be taken that no fluid bypasses the sample through an imperfect seal between the sample and the walls of the sample holder or between the sample and the supporting material if it is mounted.

d. Penetration of the mounted samples by the mounting material must be minimized by the choice of material or relatively high melting point or by careful coating of the sample. The sample should not extend beyond the surface of the mounting material. The mounting material should not be allowed to encroach to any extent upon the faces perpendicular to the path of flow. Reference to specific details of one method for sample mounting, as well as mounting materials, can be made to Par. 60 of *API RP 27*.[7]

e. The use of potting material or mounting pitch which is too brittle may tend to pull the cores apart and develop cracks on cooling. Further, the use of temperatures excessively high may burn the mounting material, leading to its decomposition and penetration of the core by some of the constituents. Also, too high a temperature in mounting these cores may result in the alteration of some samples containing clays or other hydratable minerals.

f. The desiccant used in the scrubber to dry the air of the permeameter should be checked frequently and renewed when necessary.

g. The cross section of the samples should be as uniform as possible.

APPENDIX

3.5.15A1 A METHOD FOR CASTING CORE SAMPLES IN PLASTIC

The following procedure has been used by one laboratory for successfully mounting over 50,000 cores. Epon 864 is heated until it becomes a liquid. It is then mixed with 18 percent by weight of the final mixture of dibutylphthalate. When this mixture cools, it has a consistency of molasses and has a long shelf life. Consequently, large batches of about 5 gal are prepared. When cores are to be mounted, about 20 grams of the plasticized Epon for each core are heated to between 120 and 140+ F. It is then quickly mixed with 5 cc of diethylene triamine for each 100 grams of plasticized Epon and poured around the core.

A short section of steel tubing which has been given a slight taper by pressing over a tapered mandrel is used as a core mold. The steel tubing is dipped into 50-percent silicone (Silicone 20) solution to prevent the plastic from sticking to the steel. The plastic-mounted cores are pressed out of the molds after setting by means of a modified bottle capper.

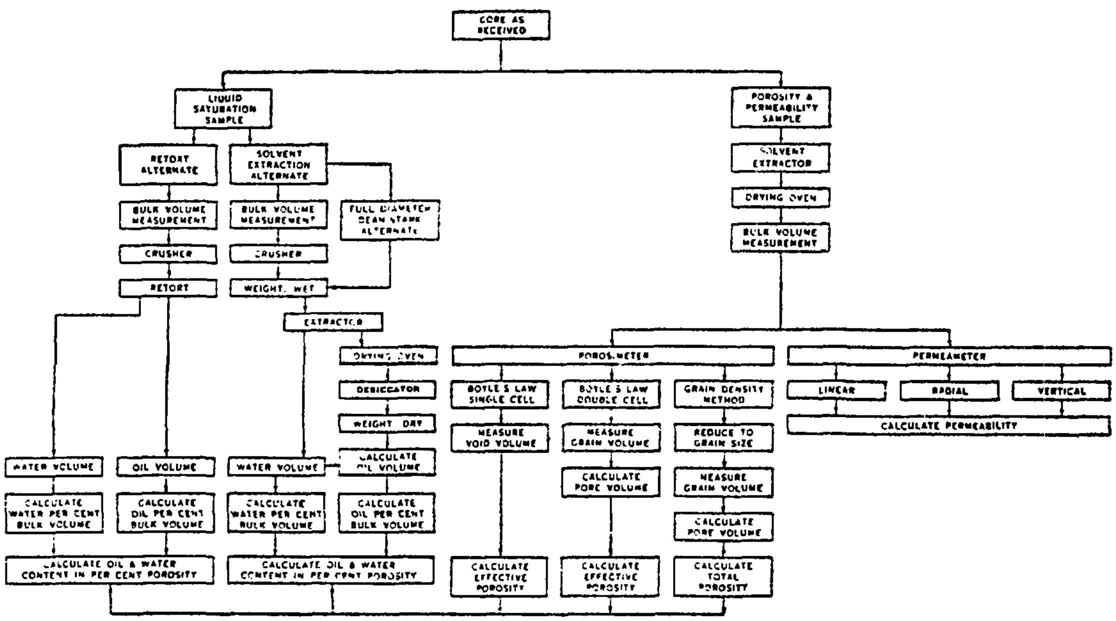
If it is desired to set the plastic rapidly, it may be heated as high as 180 to 190 F. However, if this is done, small batches must be used and the mixing of the diethylene triamine and the pouring accomplished quickly since the plastic will set in 3 to 5 min after the addition of amine.

If the plastic is handled properly, it can be cast around the core so that the penetration is not more than 1 grain thickness. In the cases of very permeable cores mounted with hot thin plastic, some invasion can occur and the penetrated area must be subtracted from the measured cross-sectional area. Some other plastics can be used, but these precautions should pertain.

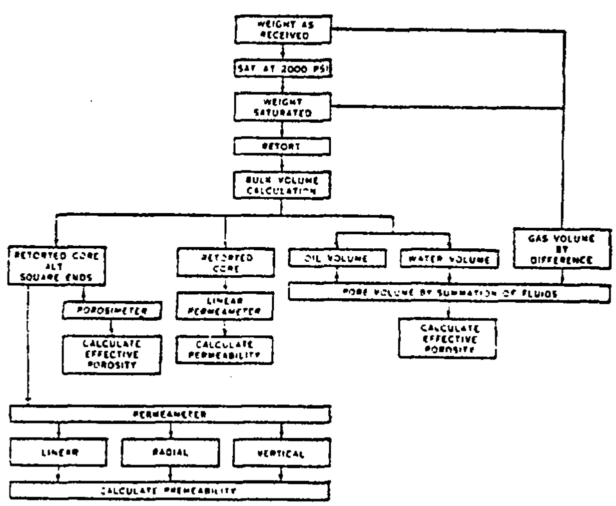
4.0. FULL-DIAMETER CORE ANALYSIS

FULL-DIAMETER CORE-ANALYSIS PROCEDURES

SOLVENT EXTRACTION



VACUUM RETORT



(A schematic flowsheet of the routine core analyses described in Section 4.1.)

4.1 LABORATORY CORE PREPARATION

The preparation of core samples for laboratory analytical procedures must, of necessity, be dependent upon:

a. The data desired on the particular core to be analyzed.

b. The type of rock or formation from which the core was taken.

c. The coring technique involved in cutting and bringing the core to the surface.

For example, if fluid-saturation data are required, the core must be carefully and expeditiously handled in the laboratory so that the fluids in the sample remain relatively undisturbed until the analysis has been undertaken. Many formations contain clays which are susceptible to swelling or chemical reaction when contacted with fresh water, thereby altering the basic characteristics (porosity and permeability) of the rock. Therefore, any fluids which contact the samples during cutting and handling of the sample prior to analysis must not in any way damage the sample or displace any of the native fluids in the sample. Prolonged exposure to sunlight, air, or heat will greatly affect the fluid saturations in the sample prior to analysis. It is, therefore, important that the samples by analyzed as soon as the preservation medium has been removed.

4.11 CUTTING OF SAMPLES

The maximum length of the core sample is dependent upon the apparatus to be used for extraction and the subsequent testing to be done.

4.12 CLEANING OF SAMPLES

Cleaning full-diameter cores requires considerably longer than the time required for conventional core samples. The core is considered to be clean when the solvent or solvents are clear after contact with the sample. If after drying the sample shows oil discoloration, the cleaning process should be repeated.

4.121 Solvents

Prior to the laboratory measurement of porosity and permeability, the original liquids must be completely removed from the core sample. Various solvents used for hydrocarbon extraction purposes, are listed alphabetically.

a. Acetone
b. Benzene
c. Benzene-methyl alcohol
d. Carbon tetrachloride
e. Chloroform
f. Ethylene dichloride
g. Hexane
h. Naphtha
i. Tetrachloroethylene
j. Toluene
k. Trichloroethylene
l. Xylene

The particular solvent to be used should be selected in order not to attack, alter, or destroy the structure of the sample. It should be recognized that the solvents in this list may not be complete solvents for all hydrocarbon constituents in natural cores, but they have been widely used for extracting samples for routine analysis. Some will be more suitable than others for specific uses; e.g., chloroform has been found to be excellent for many Mid-continent crudes, and toluene has been found useful for asphaltic crudes. Carbon tetrachloride may hydrolyze during extraction, forming hydrochloric acid as a product. When subjected to higher temperatures it decomposes, liberating phosgene gas and leaving an insoluble material in the core.

Closed-type electrical heaters should be used whenever inflammable solvents are used. Safety precautions — such as adequate ventilation of the laboratory, accessibility of fire extinguishers, fire buckets, and safety showers — should always be observed. Extraction should be conducted under hoods equipped with forced-draft ventilation.

The various solvents used for extracting core samples can be reclaimed by well-known physical and chemical methods. Such recovery can make more practical the use of an expensive solvent that is ideally suited for a particular extraction.

4.122 Gas-driven Solvent Extraction (U. S. Patent No. 2,617,719)

In this method of cleaning, the core is subjected to repeated cycles of internal dissolved- or solution-gas drive until the core is cleaned of residual oil. This method will clean any porosity, regardless of the type or complexity. It works in a crack or fissure system as well as in pure inter-granular porosity. It is successful in the so-called dead-end or one-opening type of porosity. After solvent extraction the cores are oven-dried to remove residual water and solvent.

Carbon dioxide is excellent for solution gas because of low fire or explosion hazard and high solubility in most solvents. Some of the solvents which can be used are naptha, benzene, toluene, or a mixture of solvents.

Data showing the number of cycles necessary to clean full-diameter cores for four different types of formations are presented in Fig. 4.51F1, which shows a plot of cleaning cycles vs. porosity for an inter-granular type lime, a fractured lime, a relatively clean sand, and a shaly sand. The core samples reported here were cleaned and dried and the porosity determined. They were then subjected to additional cleaning cycles and dried each time until the pore volume showed no increase.

The minimum number of cleaning cycles (5) was required for the clean sand, and the maximum number of 14 was required for the shaly sand. The fractured lime required only 6 cycles, whereas the inter-granular lime required 8. Because of the fracture system, the cleaning solvent was able to penetrate to the center of the core more easily in the fractured lime than in the inter-granular lime which had no fracture system. All samples were broken open after the cleaning experiment and examined under an ultraviolet lamp. There was no fluorescence, which is additional proof of the efficiency of this cleaning process.

The apparatus and procedure are described in 4.51.

4.123 Distillation-extraction Method

The discussion and description of this technique will be found in 4.22 and 4.53.

4.13 DRYING

Full-diameter cores may be dried in:

a. A conventional controlled-temperature oven utilizing a maximum temperature of 240 F.

b. A vacuum controlled-temperature oven utilizing a maximum temperature of 200 F.

All core samples should be dried until the weight becomes constant. The minimum time for drying full-diameter cores may be considerably longer than the 2-hour period used for conventional samples.

4.14 PRECAUTIONS

There are a number of precautions which must be observed in the preparation of all types of samples for routine core measuresments. These are:

a. Core samples containing clays and gypsum must not be dehydrated during preparation.

b. The usual criterion for sample cleanliness is a clean extract, but it must be recognized that many solvents are not complete solvents for all types of oils.

c. Heavy asphaltic oils usually require the cycling of more than one solvent.

d. Care must be exercised in drying samples containing hydrated or hydratable materials and, in some cases, temperatures lower than those indicated in 4.13 must be used.

4.2 FLUID-SATURATION DETERMINATION

Accurate determination of the fluid content and specific fluid saturations of cores is an important element in the interpretation of core-analysis data. Proper care in handling and preservation of the core until analyzed is very necessary to prevent changes in fluid content by drying or contact with water.

Specialized analytical techniques have been developed for the study of core samples of different physical characteristics and different sizes, as obtained by the various methods of coring. Several widely used procedures for determining core fluid saturations provide acceptable data.

4.21 VACUUM OR RETORT METHOD

4.211 Principle

The vacuum distillation or retort method of determining the fluid content of cores is based upon the removal of liquid from a core sample by heating and vaporization under controlled conditions of temperature and reduced pressure. The vapors are condensed, the liquids collected in calibrated glass tubes, and the volume of each liquid is read directly. Before retorting, the gas space is saturated with water. From the volumes of fluids obtained, the fluid saturations of the sample can be calculated with the aid of some other related measurements.

4.212 Data

The weight increase during the saturation step is taken as a measure of the pore volume of the core occupied by gas when the core was sampled. The amount of pore water in the sample is then calculated as the difference between total water recovered and the water injected into the sample during the saturation process. Measured oil-recovery volumes are corrected for vapor losses, cracking, and coking by using appropriate corrections determined from blank and calibration tests. The grain volume of each sample is obtained by dividing the weight of the dry sample by its grain density, determined on a representative portion or available from earlier determination. The sum of the grain volume, the total recovered-water volume, and the oil volume, gives the bulk volume. The volume of pore water, gas volume, and corrected oil volume are expressed first as percentages of the bulk volume as divided each by the sample bulk volume. A summation of these bulk-volume percentages yields the porosity of the sample. The oil and water saturations are calculated by dividing the percent volume of oil and percent volume of water by the porosity of the sample.

4.213 Advantages

a. Large samples can be used, thus providing a more representative section of the formation being analyzed, particularly where the formation is nonhomogeneous because of vugs, fractures, or heterogeneous lithology.

b. The method is relatively rapid.

c. All fluid-content determinations are made on the same sample. Each fluid-content determination is made independently of the others.

d. Samples whose minerals are stable up to 450 F. are not destroyed by the technique.

4.214 Limitations

a. The method is capable of accurate water-content determinations if the sample minerals are stable up to 450 F. If they are not — as in the case of clays, some shales, and gypsum, the water content determinations will be high.

b. Oil correction data should be determined for each crude encountered.

c. Low-gravity crude oils are difficult to distill at the temperatures used.

d. Some coking may occur when retorting weathered cores or cores containing low-gravity crude oils.

The apparatus and procedure are described in 4.52.

4.22 DISTILLATION-EXTRACTION METHOD

4.221 Principle

The method involves distilling water from the sample, condensing it, and accumulating it in a calibrated receiving tube. The oil is removed by solvent extraction and the oil content is calculated from weight-loss data and the water-content data. The method is similar to the distillation-extraction method for conventional core samples, except that the equipment is scaled for the larger core samples.

4.222 Data

The total of the several volumes of water drained from the separator bulb is the water content of the sample. The loss of sample weight, less the amount of water measured during extraction, is the weight of the oil that was contained in the sample. The oil weight is converted to oil volume with the use of the oil density. The oil and water saturations are determined with the use of the foregoing data and with porosity of pore-volume data determined in other tests.

This method lends itself to the determination of pore volume by the summation of fluids method (U. S. Patent No. 2,345,535), with little additional time involved, if the fresh samples are saturated with water before they are extracted. The weight increase during saturation is taken as a measure of the gas content of the sample. The total water extracted from the sample, less the weight increase during saturation, is the water content of the sample. The oil content is then determined (as above); and the summation of the gas, water, and oil content yield the pore volume of the sample.

4.223 Advantages

a. The procedure is simple and requires little attention during the distillation.

b. Relatively low temperatures are normally used and the decomposition of minerals is minimized.

c. Very accurate water-content determinations can be made.

4.224 Limitations

a. A long time may be required to complete the analysis.

b. Grain loss, incomplete water distillation, water gained or lost from the condenser, and incomplete drying may critically affect the oil-content determination.

c. Heating at 240 F. may cause the dehydration of clay minerals or gypsum in the sample. This will also affect the oil-content determination.

The description of the apparatus and procedure may be found in 4.53.

4.23 FLUID SATURATIONS FOR CORES CLEANED BY GAS-DRIVEN SOLVENT EXTRACTION (U. S. Patent 2,617,719)

A sample, adjacent to the section cleaned for porosity and permeability measurements, is crushed and treated by one of the techniques used for conventional core analysis under 3.2. A larger sample of core than that usually used for the conventional routine analysis may be crushed to obtain a more representative sample.

4.3 POROSITY DETERMINATION

Full-diameter core analysis is probably the most reliable method of measuring the properties of heterogeneous formations, such as vuggy or fractured carbonates or laminated shales and sands. These features, however, are those most likely to cause errors in core-analysis measurements. Vugs and fractures limit the accuracy of bulk-volume measurements by liquid-displacement techniques. In samples having distinct variations in lithology, such as mixtures of lime and dolomite, it is difficult to get a representative grain density from such a portion of the sample. Methods used on conventional core samples are generally applicable to full-diameter cores, with some modifications in equipment and technique. The major change required in equipment is a scaling up in size. Some of the procedures lend themselves better than others to dealing with the problems of the larger and usually more heterogeneous samples. With the additional stipulation that the foregoing restrictions apply, the advantages and limitations of the procedures listed under 3.3 can be used as a guide in selecting the proper bulk-volume and pore-volume measuring techniques. The porosity is determined as a ratio of the measured values for the pore volume and the bulk volume.

4.31 BULK-VOLUME MEASUREMENT

The methods most often used and probably most applicable to full-diameter core bulk-volume measurements are: *a*, liquid displacement; *b*, calipering; and *c*, summation of grain volume and pore volume. If the liquid-displacement method is used, care must be taken to fill or cover any vugs or large fractures present on the external faces of the core. This may be done with wax, plastic, clay, or tape. If an actual coating is used, its volume must be subtracted from the apparent bulk volume to yield true core bulk volume. The volume of the coating may be determined either by weighing the core before and after coating and dividing the weight difference by the density of the coating or by routinely measuring the bulk volume of the coating after it has been taken off the core. Further details will be found in 3.314 and 3.3221.

4.32 PORE-VOLUME MEASUREMENT

The pore-volume measurement may be made either as: *a*, total pore volume on a crushed sample; or *b*, effective pore volume on the uncrushed core.

4.321 Total Pore Volume

The total pore volume is the difference between the bulk volume and the grain volume. An accurate grain-density measurement is necessary for calculating the grain volume from the weight of the sample. In heterogeneous core samples, great care should be taken to obtain representative portions of the core for grain-density measurements. In some laboratories where flood-pot analyses are made or radial permeability is measured, a hole is drilled vertically through the center of the core. This drilled-out portion is normally as representative a sample as can be obtained and may be used for grain-density measurement. The procedures for grain-density measurement are described in 3.3211, 3.3212, 3.58, 3.59, and 3.5.11.

4.322 Effective Pore Volume

Many of the conventional core-analysis techniques may be used to determine effective pore volume of full-diameter cores. However, it may be impractical to scale up some of the equipment used in the conventional techniques, e.g., the glassware used in the Washburn-Bunting method. Some procedures may have to be modified to a greater degree than others.

The effective pore volume can be obtained in two ways, viz., by *a*, measuring the grain volume and subtracting it from the bulk volume; or by *b*, measuring the pore volume directly, using a modified Boyle's Law single-cell procedure or summation-of-fluids procedure.

4.3221 Grain-volume Measurement

The grain volume of full-diameter cores can be measured using a Boyle's Law double-cell procedure similar to that described for conventional cores (3.3221 and 3.5.11). Some modification of the apparatus will be necessary to accommodate the larger core sections.

4.3222 Void-volume Measurement

4.32221 Boyle's Law Single-cell Method

A description of a Boyle's Law single-cell procedure, for full-diameter cores, is presented here to illustrate the necessary modification from a conventional core-analysis procedure.

4.322211 Principles

The effective pore volume of a core may be obtained by the use of a single cell in conjunction with a gas-expansion technique. The pore volume is measured with the core mounted between two pistons. Enclosure around the core is provided by a pressurized rubber sleeve. The sleeve is fitted with an opening through which gas is introduced to the core. Pressure readings are made as gas is expanded from a known volume into the core which is originally at atmospheric pressure. The total volume into which the gas is expanded is calculated from these pressure measurements. The pore volume is defined as the difference between this total gas space and the calibrated volume of the cell. This pore volume represents the effective void volume of the core.

4.322212 Advantages

a. This method is highly precise if the system is well-calibrated and sufficient time is allowed for pressure equilibrium.

b. The sample is not damaged or altered.

4.322213 Limitations

a. The procedure is time-consuming.

b. The ends of core must be faced to provide a sample in the shape of a right cylinder.

c. Irregularly shaped cores cannot be measured.

d. Large vugs must be covered with shim stock or filled with clay to serve as support for the rubber sleeve.

The procedure should be accurate to within ±3 percent of the pore volume measured for pore volumes less than 20 cc, ±1 percent or less for pore volumes greater than 20 cc.

4.32222 Summation of Fluids
(U. S. Patent No. 2,345,535)

In the determination of effective pore volume by summation of fluids, the recommended technique for full-diameter cores is to obtain both liquid and gas saturations from one piece of core. This permits the use of a larger sample for the measurements. The core is saturated with water before retorting, to measure the gas volume by calculation from the increase in weight during saturation. The pore water is then calculated as the difference between the total water distilled from the sample and the water used to saturate the sample. The pore volume is the sum of the measured gas, water, and oil volumes.

Further details of the procedure can be found in 4.52.

4.4 GAS-PERMEABILITY DETERMINATION

Permeability is a measure of the ability of a porous sample to transmit fluids. Either gases or liquids are used as fluids in permeability measurements. However, liquid permeabilities are not considered routine because of such factors as interaction between rock constituents and liquids and control of bacterial action. Therefore, only gas permeability will be considered in this recommended practice.

The permeability measurement will be standardized sing dry air as the gas. If air permeabilities reported or routine core analysis have been corrected, using a standard table of Klinkenberg corrections,[7] then this should be noted specifically in the report. This corrects the gas permeability of a porous medium to the corresponding value for a non-reacting liquid. This correction is most important for samples with low permeability. The direction parallel to the bedding plane will be standardized as the horizontal permeability. Any measurements in other directions, i.e., vertical, should be so specified and the details described.

Samples of hard, consolidated cores are run according to either the conventional or full-diameter scheme, depending upon their nature. Vugular, fractured, or crystalline carbonate rock, fractured and recemented cherts, and laminated shaly rocks are often best handled by full-diameter methods to obtain a more representative permeability value for the interval tested.

4.41 GENERAL PROCEDURE

The core sections selected for testing are cleaned as described in Section 4.1. If the cores have been tested for fluid-saturation measurements, they will not contain water or hydrocarbons and can be used directly for permeability tests. If samples have contained very saline water, it may be necessary to remove salt from the samples before permeability is measured.

Two methods of measuring permeability on full-diameter cores are common. One method, usually referred to as "linear permeability measurement", utilizes either a Hassler-type holder or a compression, ram-type holder to measure horizontal permeability. These units permit vertical permeability measurements if desired. The second method is designated s "radial permeability." In this method the air is dmitted to the outside diameter of the core and the rate of flow through the core into a small hole drilled in the center is measured. Measurements of air flow through the sample are made with the orifice-manometer arrangement described for conventional core analysis (see 3.5.15.2b).

4.42 LINEAR PERMEABILITY MEASUREMENT

4.421 Principle

Linear full-diameter core permeability measurements utilize either a Hassler-type holder or a unit employing two rubber cradles and a hydraulic ram (or compression-type holder) to seal the core sample. Screens are used to distribute the air flow uniformly over the upstream section of the core and to allow uniform flow of air from the core. Both procedures are based upon the same principle and yield comparable results. Horizontal permeabilities are normally measured in two directions across the core diameter. If only one direction is measured, it should be with the direction of principal fracturing, if any. The second measurement is normally in a direction perpendicular to the direction of the first measurement. The apparatus and procedures are described in 4.55.

4.422 Advantages

a. The linear full-diameter measurement provides a maximum length for the flow path of the air.

b. Measurements can be made in various horizontal directions giving a better matrix evaluation.

c. Both vertical and horizontal permeabilities can be measured.

4.43 RADIAL PERMEABILITY MEASUREMENT

4.431 Principle

The permeameter consists essentially of a double piston, with the lower piston somewhat larger in diameter than the upper one, so that air pressure applied to the lower chamber will overcome any pressure exerted by air in the upper or specimen chamber.

The faced core specimen with a vertical center hole is sealed in position in the upper chamber by air pressure in the lower chamber. One end of the vertical hole is sealed and the other end is open to the flowmeter. The upstream air is allowed to enter the specimen chamber at measured pressures, the downstream pressure and flow recorded, and the permeabilitity factor calculated from Darcy's radial-flow formula.

Vertical permeabilities may be measured in other full-diameter equipment prior to drilling the center, vertical hole.

Details of the apparatus and procedure may be found in 4.56.

4.432 Advantages

a. The center sample provides material for grain density and porosity measurements.

b. Cores prepared for radial permeability measurements may be used for flood-pot tests.

4.433 Limitations

a. Fractured materials may fall apart when drilled.

b. The length of the sample is restricted to that which may be drilled with a straight hole.

4.5 DESCRIPTIONS OF METHODS FOR ANALYSIS

4.51 GAS-DRIVEN SOLVENT EXTRACTION (U. S. Patent No. 2,617,719)

4.511 Apparatus

Because a diagrammatic sketch is quite complex, reference should be made to the above patent for modifications in the apparatus from that used in conventional core analysis (3.521).

4.512 Procedure

The cores are placed in a high-pressure chamber. The chamber is pressured up with gas to a pressure equal to that of the gas dissolved in the solvent (200 psi). The gas in the chamber is then displaced at constant pressure by the solvent containing the dissolved gas. After the chamber is filled with this solvent, it is pressured by means of a hydraulic pump to approximately 4 or 5 times the pressure of the gas dissolved in the solvent (1,000 psi). When liquid flow into the core ceases, the core chamber is rapidly depressured to atmospheric pressure and the core left submerged in the solvent until most of the gas has flowed from the core. The solvent is then drained from the chamber and the cycle repeated. Pressure and drain periods are repeated until visual observation indicates the cores are clean. This cleaning operation is more effective when the high-pressure chamber is heated to 160 to 180 F. — electrically, by steam, or by hot water.

The cores are then dried in an oven (see 4.13) and inspected again to determine whether further cleaning is necessary. A thorough cleaning is indicated when the cores have no oil stains on the surface after drying.

4.513 Data

Data showing the number of cycles necessary to clean four different types of full-diameter cores at room temperature are shown in Fig. 4.51F1. Samples from formations bearing only gas or distillate, where no oil stains could indicate the degree of cleanliness, have been found to be clean after 3 cycles.

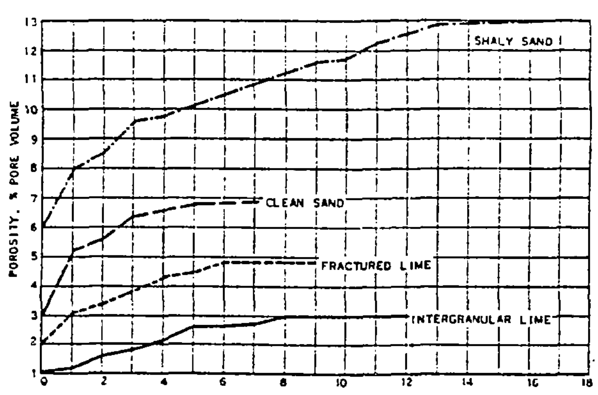


FIG. 4.51F1 — DATA SHOWING NUMBER OF CYCLES NECESSARY TO CLEAN 4 DIFFERENT KINDS OF FORMATIONS

For a relatively clean, permeable core 6 to 8 cycles may be sufficient, depending upon the the nature of the oil in the cores. For low-permeability cores containing low-gravity crude, 20 cycles may be sufficient when the high-pressure chamber is heated; whereas as many as 40 cycles may be needed at room temperature.

Consideration of the type of crude in the sample is always important in determining the number of cycles necessary for cleaning. In any one type of porosity, a low-gravity crude will require more cycles than a high-gravity crude.

4.52 VACUUM-RETORT METHOD

4.521 Apparatus

The equipment to perform the vacuum distillation process must include a heating chamber which will contain the sample, a condensing system or cold bath, a receiving tube for the liquids, and a vacuum system to the condenser and heating chamber. Fig. 4.52F1 presents an example of such a system. The heating chamber in a system in general use is an aluminum-alloy cylinder whose inside dimensions are 6 in. in diameter and 24 in. long and which is closed at one end. The aluminum cylinder is contained in a stainless-steel shell which houses three thermostatically controlled electrical heating elements. The thermostat control can be adjusted to various temperatures. Normally, 10 such chambers are built in one housing. The temperature of each chamber is controlled independently and any chamber may be removed from the system if not needed. Inside the chamber the core sample is held away from the chamber walls in a wire-mesh tray to insure better heat distribution to the sample and to allow the heavier oils to flow unrestricted to the outlet. The open end of the chamber is closed with a flat lid containing an outlet pipe. The lid is sealed with a silicone rubber O-ring and clamped into placed with wingnuts on studs.

The outlet tube from the chamber lid conducts any flowing liquid and the vapors into a calibrated glass receiving tube. The outlet tube and receiving tube both act as the condensing system. The glass receiving tube is maintained in a cold bath of alcohol and dry ice (temperature approximately —75 F.). At this temperature the vapors are condensed or frozen in the glass receiving tube.

A vacuum pump connected to the glass receiving tube reduces the pressure throughout the distillation system. Pressure, as well as temperature, is controlled on the system to maintain a proper vaporization rate. A mercury manometer indicates the total pressure on the system during the operation.

4.522 Procedure

Prior to the vacuum distillation operation, the core is divided into samples of 6 to 22 in. in length. Care should be taken during sampling to prevent fracturing of the core. The samples are marked for identification and weighed to obtain the unsaturated or natural weight. The samples are evacuated to remove the gas and are then saturated with deaerated water at a pressure of 2,000 psig. Evacuation periods of 5 to

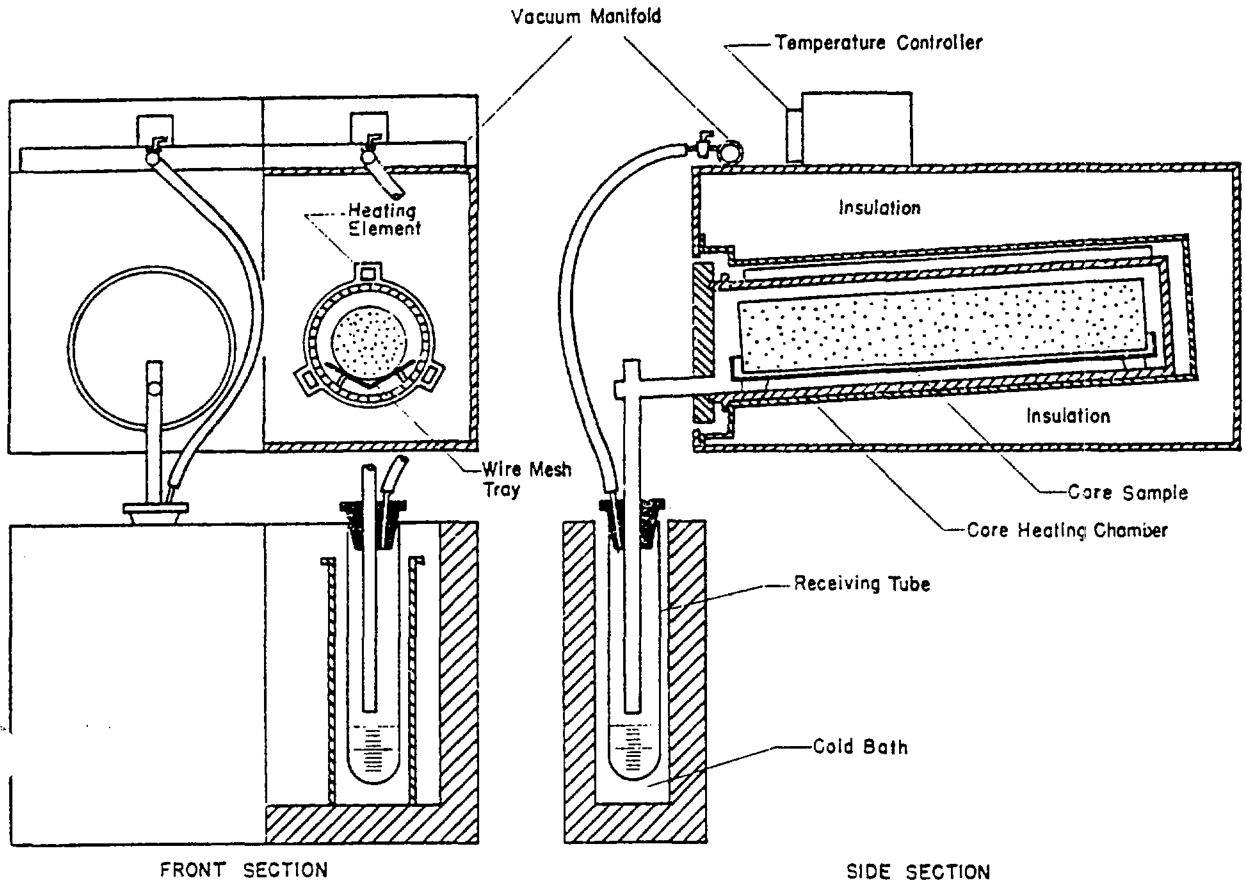


FIG. 4.52F1 — VACUUM RETORT

10 min have been found adequate to reduce the pressure to that of water vapor at ambient pressure. Further evacuation may cause volatile liquids to be lost from the core. Water-saturation periods vary from ½ to 1 hour, depending upon the permeability characteristics of the samples. The samples are removed from the saturator, and the weights of the saturated samples are obtained.

The samples are then placed in the vacuum distillation apparatus. The lids are checked for proper vacuum sealing and then tightened with wingnuts. A calibrated glass receiving tube is placed on the outlet pipe and the alcohol cold bath is raised to cover the glass tube. The alcohol bath must be approximately —75 F. before the beginning of the heating operation. Pressure on the chambers is reduced by using the external vacuum pump. The distillation process may be varied somewhat for the type of sample, but usually the temperature is controlled at approximately 300 F. and the pressure in the chamber is maintained between 200 mm Hg and 300 mm Hg at the beginning of the distillation process. This condition in the chamber is held until the bulk of the sample fluids are distilled over, which usually is within 2 hours. The temperature is then increased to approximately 450 F. and the maximum vacuum applied until all the liquids are distilled or flow out. The distilled fluids are condensed and collected in the calibrated glass receiving tubes which are maintained in the alcohol-dry-ice bath. Because of the extremely low temperature, the water and oil are frozen and essentially no vapor is carried into the vacuum system. The total distillation time varies from 4 to 8 hours, depending upon the characteristics of the samples. After distillation has been completed, the receiving tubes are removed and thawed in a warm-water bath. The water bath must be warm to prevent breakage of the glass receiving tubes by expansion of the ice. The volumes of water and oil obtained from each sample are recorded. The samples are weighed after the vacuum distillation is completed to obtain the "dry weight".

4.53 DISTILLATION-EXTRACTION METHOD

4.531 Apparatus

Fig. 4.53F1 illustrates an apparatus used for the distillation of the core samples. It consists of an electrically heated oil bath, a chamber to contain the core sample and solvent, an offset condenser to condense the water and solvent vapors, and a refluxing trap that will allow the condensed solvent to reflux into the core chamber. The individual sample chambers may be placed in separate heating baths, but normally several of them are placed in a common heating bath. The sample chamber is usually made of aluminum tubing with an inside diameter of 5 to 6 in., depending upon the maximum size of core analyzed. The length of the pot is normally from 15 to 24 in. The bottom end is closed with a welded plate and the top has a flange for bolting on the lid.

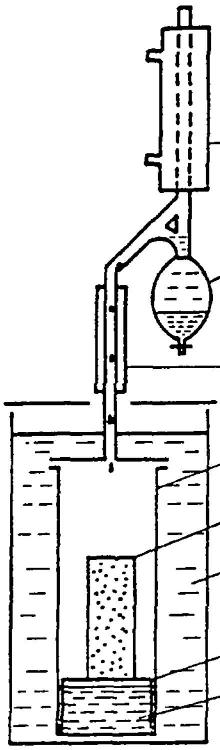


FIG. 4.53F1 — DISTILLATION EXTRACTION APPARATUS

The lid is bolted to the chamber. A gasket between the two sections provides a vapor-tight seal. The chamber lid, in turn, is connected to the condenser-trap assembly with a gasketed union. The lower portion of the condenser is wrapped with insulation to prevent premature condensation of the vapors.

A glass separator bulb is normally used to collect the distilled and condensed water since the volume of water distilled from the core sample is often large. The water collected in the separator is drained from time to time. Care must be taken to prevent water hang-up in the condenser and trap. The inside of the bulb may be coated with a silicone compound to eliminate or minimize hang-up of water. A calibrated glass receiving tube is used to measure the volume of water drained from the bulb. With smaller samples, a calibrated receiving tube can be used in place of the separator bulb.

4.532 Procedure

The core is divided into samples 6 to 22 in. in length. The samples are marked for identification and weighed to obtain the wet weight. The samples are placed into the core chamber. Enough clean, water-free toluene is added to the chamber to insure good refluxing action. A gasket is placed on the chamber flange, and the lid is bolted in place. The loaded chamber is placed in the heating bath and is connected to the condenser-trap assembly. The temperature of the heating bath is raised to approximately 240 F. As it becomes necessary, water is drained from the separator bulb into a calibrated receiving tube, and the water volume is recorded. The process is allowed to continue until 1 cc of water, or less, is distilled from the sample in a 24-hour period. This may require from 3 days to 3 weeks. The core chamber is then taken from the heating bath and opened. The core is dried in an oven to remove the solvent from the sample. The dry weight of the sample is taken.

4.54 BOYLE'S LAW SINGLE-CELL METHOD FOR POROSITY

4.541 Apparatus and Equipment Calibration

a. Rubber-sleeve cell with hydraulic jack.
b. Reference volume and manifold.

Two separate volumes from which gas can be expanded into the core may be used. These gas sources are the manifold and the reference volume shown in Fig. 4.54F1. A steel nipple or pipe with one end capped may be used for the reference volume. The manifold may be made up of small metal tubing and various fittings. The chamber for the reference volume must be independently calibrated. This can be done gravimetrically with distilled water. This chamber may then be used to calibrate the manifold by

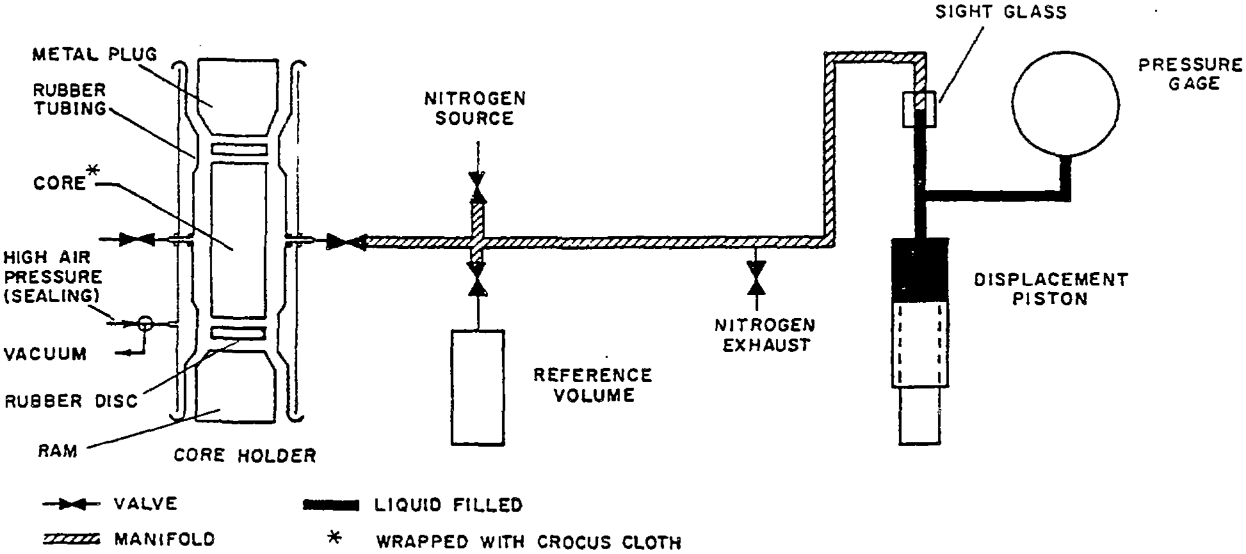


FIG. 4.54F1 — *PORE-VOLUME APPARATUS*

means of gas expansion. If temperature fluctuations in the laboratory are not great, temperature corrections may be negelected. The combined volumes of the manifold and reference volume, or the manifold volume alone, should approximate the pore volume to be measured. This allows pressure measurements to be made within the most accurate limits of the gage while obtaining a maximum pressure drop.

c. Gage level indicator and displacement piston.

The gage level indicator is a plastic block with an etched reference line. The oil level in a line connecting the block and gage indicates the contraction and expansion of the Bourdon-tube pressure gage. A displacement piston is placed between the level indicator and the gage so that the oil level may be held constant at the etched line. This insures a constant manifold volume.

d. Pressure gage (normally 0-100 psi Bourdon-tube test gage).

e. Vacuum source.

A vacuum is normally applied to the outside of the sleeve whenever it is moved relative to the core and the pistons. This provides greater clearance between the sleeve and the core, thus protecting the sleeve from damage.

f. Crocus cloth.

This is to aid distribution of the gas over the surface of the core in order to reduce the time required for pressure equilibrium. It is prepared by rubbing it against a similar sheet to remove the rough grit surface. The pore space in the cloth is approximately 0.075 to 0.08 cc per sq in. Therefore, the area of the cloth surrounding a core must be measured to determine the volume contributed by it in the cell.

g. Regulated source of pressure.

Dry, clean nitrogen may be used since the compressibility factor remains essentially unity over the temperature and pressure ranges involved in the test.

4.542 Procedure

The core to be tested is cut in the shape of a right cylinder. The sides are wrapped with crocus cloth, to within ¼ in. of each end. The crocus cloth may be held in place with rubber bands. The area of the crocus cloth is then measured.

The cloth is placed in the Hassler-type cell which is equipped with two pistons, one of which is operated by a hydraulic jack. Two circular rubber pads, approximately ¼ in. thick, are placed on either end of the core and the assembly is mounted between the two pistons. The section of cell containing the rubber sleeve, which is fitted with a nipple through which the gas is expanded to the core, is placed around the core. The valve connecting the cell and the manifold is closed (see Fig. 4.54F1). The outlet valve on the cell is opened to the atmosphere. Pressure is then applied incrementally and concurrently to the outside of the sleeve and to the hydraulic jack in order to equalize the pressures applied to all surfaces of the core. A sleeve pressure of 300 psi is normally sufficient to seal the core. The jack pressure should be at least 100 psi greater than the sleeve pressure.

Gas pressure between 60 and 70 psig is introduced into the manifold and reference volume system. The oil in the sight glass is adjusted to the etched reference line by means of a displacement piston. The valve connecting the pressure source to the system is closed, and the pressure existing in the known volume of the system is recorded as P_1. The outlet valve of the cell is closed and the inlet valve, which connects the cell to the rest of the system, is opened, thereby admitting gas to the core. Sufficient time should be allowed for the establishment of pressure equilibrium. The time needed to reach pressure equilibrium varies with different cores of the same apparent horizontal permeability. This variation depends upon position, number, and size of fractures and vugs as well as on the permeability of the rock matrix. Normally, cores having an average horizontal permeability of 0.1 md reach pressure equilibrium in 15 to 20 min. Cores having a permeability of 0.1 md, or greater, reach pressure equilibrium in 10 min or less.

The position of the oil in the sight glass is again adjusted to the etched reference line and the final stabilized pressure is recorded as P_2.

4.543 Calculations

To calculate the gas volume in the cell the following formula is used:

$$V_2 = [V_1(P_1 - P_2)]/P_2 \qquad (19)$$

Wherein:

V_2 = total gas volume, in cell and core, cc.

V_1 = reference volume and manifold volume, cc.

P_1 = inital pressure of the gas in the known volume, psig.

P_2 = final pressure of the gas in the entire system, psig.

Since V_2 = *total gas volume*, then:

$$V_p = V_2 - V_c - V_k \qquad (20)$$

Wherein:

V_p = pore volume, cc.

V_c = pore volume of crocus cloth, cc.

V_k = calibration volume for the necessary valve stems and connections to the cell, cc.

The ratio of the pore volume and the bulk volume of the core, multiplied by 100, yields the effective porosity of the sample.

4.544 Precautions

a. Allow sufficient time for core to reach atmospheric pressure after applying sleeve pressure and at conclusion of test.

b. Allow sufficient time for system to reach final stabilized pressure before recording P_2.

c. Calibrate manifold volume whenever fittings are changed or alterations made.

d. Check frequently for leaks.

e. No visible gaps should exist between the ends of the core and the rubber pads.

4.55 LINEAR PERMEABILITY MEASUREMENT

4.551 Preparation of Sample

Samples which have been removed from the drying oven following the cleaning operation (see 4.12) are cooled to room temperature and marked to indicate inlet- and outlet-screen positions. The core samples are then measured by a micrometer to determine diameter and length. If rubber gaskets are used to seal the ends of the core, a diamond saw is used to make a smooth horizontal cut of each end. A square cut of this type is also required for vertical premeability measurements. When horizontal permeability only is needed, and the ram-type holder is used, the ends of the sample may be sealed by dipping them in a molten plastic material which solidifies after cooling. Appropriate-size screens are attached diametrically opposite each other by light rubber bands and then the core samples are placed in the holder. Each screen will cover one quadrant of the core circumference.

4.552 Apparatus

The holder may be either a permeameter as shown in Fig. 4.55F1, known as the compression (ram) permeameter, or Fig. 4.55F2, usually referred to as the Hassler-type permeameter.

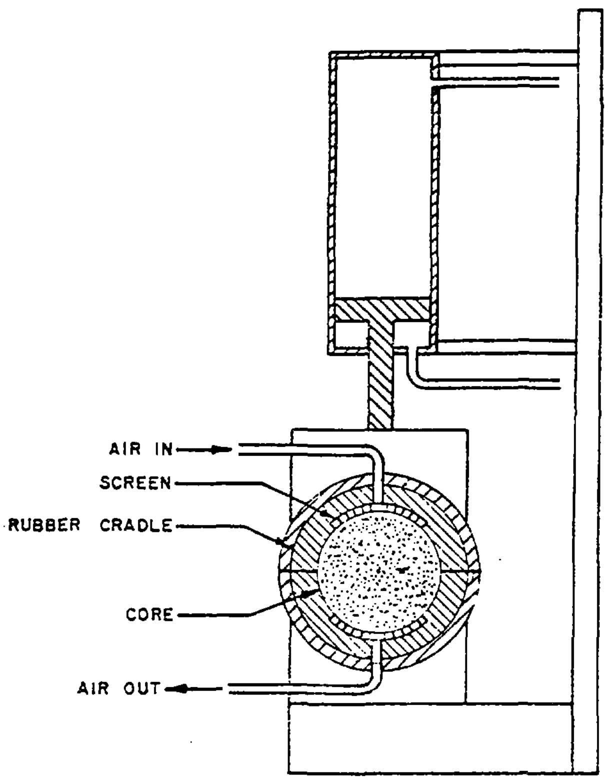


FIG. 4.55F1 — COMPRESSION (RAM) PERMEAMETER

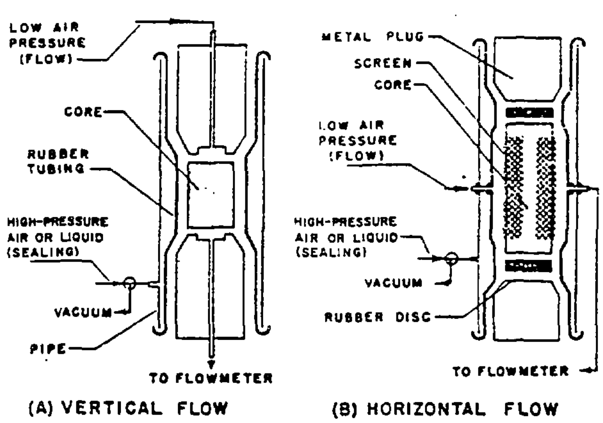


FIG. 4.55F2 — HASSLER-TYPE PERMEAMETER

The ram permeameter may be used with cores which have the ends sealed with plastic that are overlapped by the compression halves lined with soft rubber. This completely seals the outside of the core except the area covered by the screens. Air is admitted and removed from the core by two screens placed on diametrically opposite quadrants of the core sample. Permeability is normally measured in two directions — one giving the maximum value (normally along the direction of principal fracturing), and the other at 90 deg to the maximum.

The Hassler-type permeameter consists essentially of a length of steel tubing carrying a rubber sleeve in the interior. The sleeve is attached to the tubing at each end in such a way as to seal the annular space between the tube and the sleeve. Two flow tubes, diametrically opposite, allow flow across the core sample. A hydraulic ram compresses rubber gaskets which seal the ends of the sample. The rubber sleeve is pressured to seal surfaces of the cores except where the screens are positioned. Permeability is normally measured in two directions—one giving the maximum value (normally along the direction of principal fracturing), and the other at 90 deg to the maximum. Vertical permeability is determined by use of this same apparatus by removing the screens from the sides of the cores and replacing the end plugs and rubber disks with perforated end plates and rubber rings for admitting air to the core end. The vertical permeabilities can be measured by selecting the correct inlet and outlet connections.

4.553 Procedure

The measurement of air-flow rate through a sample is then taken intermittently for a period of 3 to 10 min until the flow becomes constant. Flow rates are controlled to minimize turbulence. The maximum rate is limited by the permeability and size of the sample. The rate of air flow is measured by means of a calibrated orifice and water or mercury manometer. An alternative method is measurement in the downstream outlet by timing a soap-film movement in a burette. The calculation of air permeability takes into account the cylindrical shape of the sample, the length of the sample, and the size of the screens through which the air is introduced and removed.

4.554 Calculations

Full-diameter core horizontal permeability is calculated from Darcy's equation, which has been modified by the substitution of a "shape factor." The shape factor, which can be derived from electrical models, flow tests, and geometric analysis, is based upon the diameter of the sample and the arc width of the screens used to distribute the air. The Darcy equation for linear gas flow in 3.5.15 is modified to the following form:

$$k = (Qm\mu/L\Delta P)\ (1{,}000)\ (G) \tag{21}$$

Wherein:

k = permeability, millidarcies.
Qm = volume rate of air flow at mean core pressure, cc per sec.
μ = viscosity of gas, centipoises.
L = length of sample, centimeters.
ΔP = pressure drop across core, atmospheres.
G = shape factor (when screen covers 90-deg section of the core, $G = 1.0$). The shape factor G is based on the arc width of the screens and the core diameter.[12] (See Fig. 4.55F3.)

Vertical permeability is calculated from the normal Darcy equation.[11]

4.555 Precautions

a. The permeameter should be checked regularly by means of standard samples.

b. Care must be taken that all flow is through the sample and that no gas bypasses the sample because of an imperfect seal between the sample and the sample holder. If the ends of the sample are sealed by dipping in plastic, the plastic must remain sufficiently flexible to prevent cracking and bond firmly enough to prevent loosening or bypassing of air during the test.

c. The desiccant used in the scrubber to dry the air to the permeameter must be checked frequently and renewed when necessary.

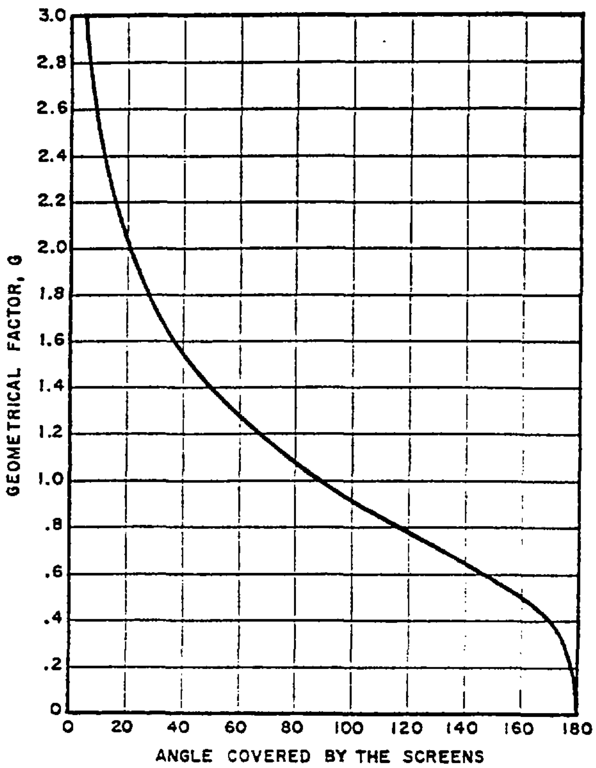


FIG. 4.55F3—THEORETICAL CURVE RELATING THE GEOMETRIC FACTOR AND THE ANGULAR SEGMENT OF THE CORE COVERED BY THE SCREENS

[Collins, R. E: *J. Appl. Phys.*, 23, 681 (1952)]

d. Care must be taken that the screens remain in proper position during compression before making permeability measurements.

e. When using the Hassler-type holder, always apply vacuum to the sleeve before moving the body of the cell.

4.56 RADIAL PERMEABILITY MEASUREMENT

4.561 Apparatus

The full-diameter radial permeameter consists of three parts: The cell, which is sufficiently large to maintain a uniform inlet pressure; the piston to apply a sealing force; and the floating plate assembly which consists of a lower fixed plate, a pivot ball, three springs 120 deg apart, and the upper floating plate. (See Fig. 4.56F1.)

4.562 Procedure

The core is placed on a 1-in. solid rubber gasket which is attached to the lower floating plate. The core is then raised against the closed lid, the center hole of the core matching that of the upper gasket. As the piston pressure increases, the lower floating plate automatically adjusts if the ends are not parallel.

To check for an air leak between the ends of the core and the rubber gaskets, the piston pressure is increased. A decrease in the flow rate indicates that a leak had existed. This test is then repeated until no change in the flow rate is noted.

The rate of air flow is measured by means of a calibrated orifice and water manometer. The air-flow rate is taken after successive readings indicate a stabilized flow. An alternative method is measurement in the downstream outlet by timing a soap-film movement in a burette.

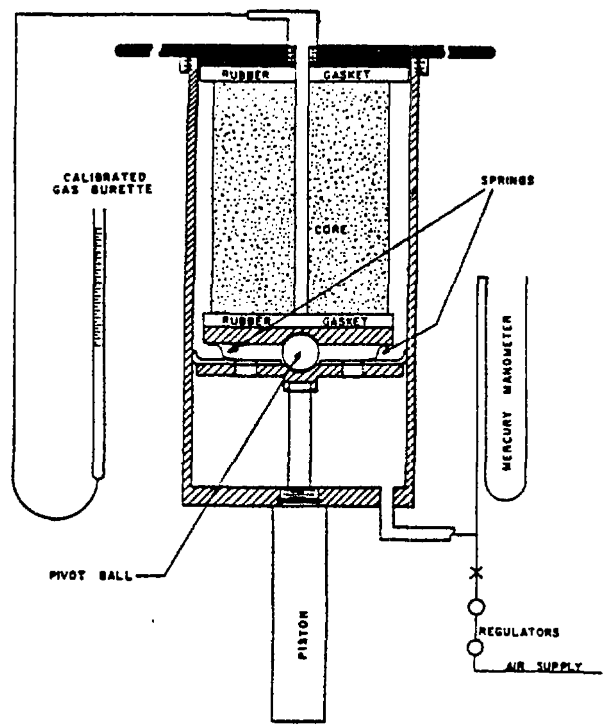


FIG. 4.56F1—FULL-DIAMETER RADIAL PERMEAMETER

4.563 Calculations

The radial permeability of the core specimen is calculated directly from Darcy's radial-flow equation. Since the height of the specimen and the height of the surface subjected to pressure are identical, there is no "shape factor."

The dry-air permeability can be calculated from the following Darcy radial-flow equation of gas.[11]

$$k = [(\mu Q_a)\ (ln\ de/dw)\ (p_o)/(\pi\ h)\ (p_i^2 - p_o^2)][1,000] \qquad (22)$$

Wherein:

- k = permeability, millidarcies.
- μ = viscosity of the air, centipoises (at test temperature).
- Q_a = measured rate of flow, cc per sec (at test temperature and at pressure = p_o).
- dw = inside diameter of inner hole, centimeters.
- de = outside diameter of sample, centimeters.
- p_i = pressure at inlet to core, atmospheres (absolute).
- p_o = pressure at outlet of core, atmospheres (absolute).
- h = height of sample, centimeters.

If $p_o = 1$ *atmosphere* and the orifices are calibrated over the range of inlet pressures, the calculation is simplified. The Darcy radial-flow equation may then be used in the following form:

$$k = [\mu Qm\ (ln\ de/dw)/2\pi h\ \Delta_p]\ [1,000] \qquad (23)$$

Wherein:

- k = permeability, millidarcies.
- μ = viscosity of air, centipoises.

Qm = volume rate of air flow at mean core pressure, cc per sec.
de = outside diameter of sample, centimeters.
dw = inside diameter of center hole, centimeters.
h = height of sample, centimeters.
Δp = pressure drop across the sample, atmospheres (absolute) = $(p_i - p_o)$.
ln = logarithm to the base *e*.

4.564 Precautions

a. The sample should be drilled on center.

b. The sample should be inspected carefully to determine whether any cracks or splintering of the sample occurred during drilling.

c. The permeameter should be checked regularly by means of standard samples.

d. Care must be taken that all flow is through the sample and that no gas bypasses the sample because of an imperfect seal between the sample and the sample holder.

e. The desiccant used in the scrubber to dry the air to the permeameter must be checked frequently and renewed when necessary.

5.0 SMALL-SAMPLE ANALYSIS

Small samples, such as large cuttings or percussion-type sidewall samples, can *only approximately approach* conventional or diamond-core samples in providing quality and quantity of formation for analysis. In view of the inherent deviations in a vertical section of any formation, several samples should be obtained from each zone if it is sampled at all. In many instances, particularly in exploratory drilling where a normal coring program may not be practical, small samples provide valuable qualitative information on formation properties which cannot be obtained in any other way after the formation has been drilled. Analytical methods have been improved with the marked increase in the amount of small-sample coring, and some measurements of the physical properties of small samples as received can now be made with satisfactory accuracy. Evaluation and interpretation of small-sample data are strengthened greatly if made with full knowledge and understanding of the properties measured with any of several available electric logs. Similarly, experience has shown that the small-sample data are an extremely important aid in proper electrical-log interpretation.

5.1 LABORATORY CORE PREPARATION

Samples too small for analysis by conventional means have limited value in respect to quantitative determinations. These include sidewall samples, chips, and bit cuttings.

5.11 CUTTING OF SAMPLES

Small samples and sidewall samples may require special handling and their laboratory preparation will be discussed in connection with the tests.

5.12 CLEANING THE CORES

The extraction of small core samples may be accomplished as described in 5.52.

5.13 DRYING

The drying of small core samples usually can be achieved in:

a. A conventional controlled-temperature oven utilizing a maximum temperature of 240 F. for a minimum of 2 hours.

b. A vacuum controlled-temperature oven utilizing a maximum temperature of 200 F. for a minimum of 2 hours.

All core samples should be dried until the weight becomes constant.

5.2 FLUID-SATURATION DETERMINATION

5.21 RETORT METHOD AT ATMOSPHERIC PRESSURE

(Use of downdraft retort covered by U. S. Patents No. 2,282,654 and 2,361,844)

5.211 Principle

The method involves removal of the total fluid content of the sample by heating at atmospheric pressure, condensing the vapors, and collecting the recovered liquids in a calibrated receiving tube. The method is very similar to the conventional method of retorting at atmospheric pressure, but the sample cups and liquid receiving tubes are greatly reduced in size to provide accuracy with the small amounts of materials involved (Fig. 5.21F1).

5.212 Data

The oil, water, and gas contents are calculated in terms of percentage of the bulk volume from the volumes of fluid recovered from the retorting and the bulk volume of the sample. The use of properly determined oil and water distillation correction curves permits determination of oil content to within 5 percent and of the water content to within 3 percent of the values measured. Examples of the water and oil calibration curves are shown in Fig. 5.21F2 and Fig. 5.21F3.

5.213 Advantages

a. One segment of sample used to determine gas, oil, and water content.

b. The method is fairly rapid.

c. Each measurement is made directly and independently of others.

5.214 Limitations

a. The distilled liquids tend to form emulsions.

b. Considerable care is required to obtain proper water calibration.

c. Very small amounts of oil may be difficult to determine accurately.

The apparatus and procedure are described in 5.51.

5.22 PENTANE EXTRACTION METHOD

5.221 Principle

The total oil content of the core sample is extracted by successive addition and decanting of small quantities of pentane. The pentane is then removed by evaporation in a constant-temperature bath, and the

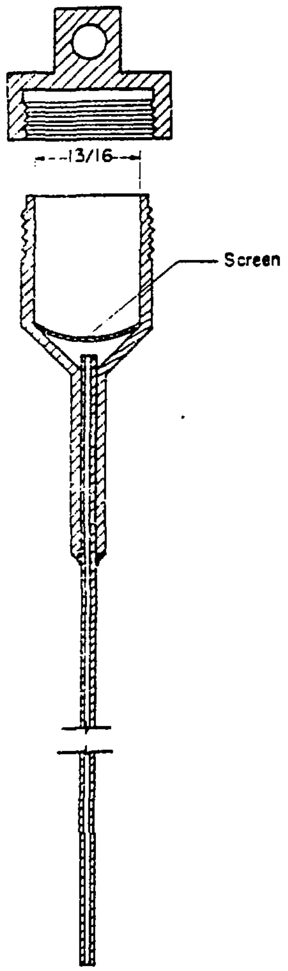


FIG. 5.21F1—RETORT CUP—SIDEWALL SAMPLE

recovered-oil volume is read directly in the calibrated evaporation tube. The water content is calculated from a material balance.

5.222 Data

The volume of recovered oil is corrected for excessive losses with the pentane, or for failure to remove all of the pentane by comparison with calibration curves, as shown in Fig. 5.52F2. The water content is then calculated as a percentage of the bulk volume of the sample by a material-balance equation, as shown in 5.523.

Oil content may be determined with an average error of ±4.5 percent of the measured volume if proper calibration charts are used. The average error in the calculated water content is of the order of ±7 percent of the measured volume.

5.223 Advantage

a. The method is rapid, and reasonably accurate results are obtained.

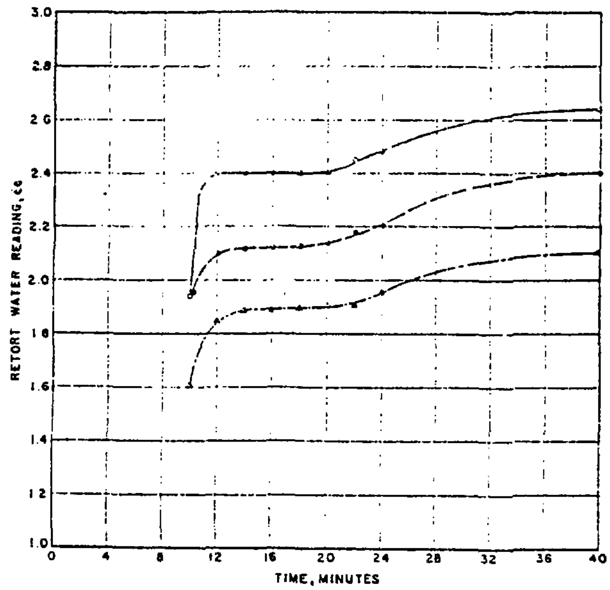


FIG. 5.21F2—WATER-CALIBRATION CURVES

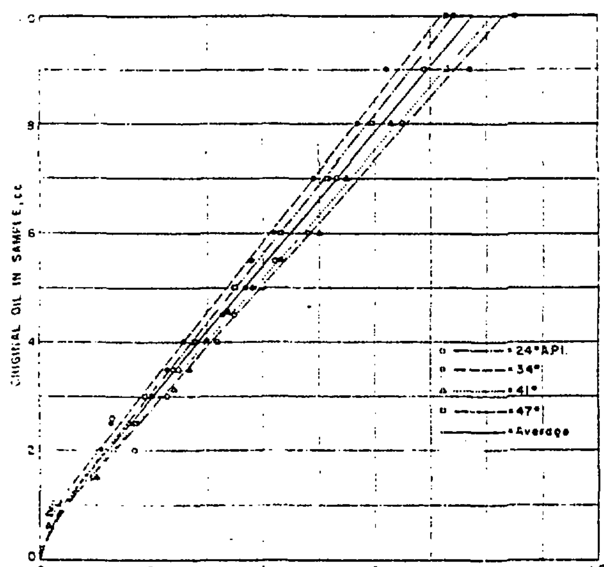


FIG. 5.21F3—OIL-CALIBRATION CURVES FOR SIDEWALL RETORT CUPS

5.224 Limitations

a. Results are sensitive to operator technique.

b. Wide variations in crude-oil properties may require calibration for various temperatures of evaporation bath.

c. Errors in grain-density value or in measurement of gas or oil content contribute to errors in calculated water content.

The apparatus and procedure are described in 5.52.

5.3 POROSITY DETERMINATION

Bulk volumes and porosities can be obtained on small samples with the same methods used in conventional core analysis. In order to effectively handle the smaller sample, it may be desirable to scale down some of the conventional apparatus. Even this scaling down may not be necessary for some equipment, however, since such apparatus as the Boyles' Law double cell, wherein the ratio of sample volume to sample-chamber volume may be critical, can be modified by simply adding steel blanks of known volume to help fill up the chamber.

The same limitations need not apply to all small samples since, for instance, some may be large enough to cut into regular shapes for calipering while others may not.

Procedural changes are greatest in the summation-of-fluids method (U. S. Patent 2,345,535), two modifications of which are presented following.

5.31 RETORT METHOD

In the retort method, the sample is cleaned of mud, placed in a mercury pump, and its bulk volume determined. The gas content of the sample is obtained by injection of mercury (see 3.533). This mercury-injected sample is then placed in a small, specially designed retort cup for distillation of liquid content. The mercury, water, and oil are retorted from the sample and condensed into a graduated collecting tube. Addition of a few drops of emulsion-breaker solution and centrifuging gives good separation of the liquids and permits accurate direct reading of their volumes. Porosity is calculated by summation of fluids (see 3.3222).

The average error in oil saturation is about ±5 percent of the saturation value. Average error in water saturation is less than ±2.5 percent of the saturation value.

A major advantage offered by this analysis is that gas content, oil content, and water content are all measured directly and on the same piece of rock.

For further details see 5.21 and 5.51.

5.32 PENTANE EXTRACTION METHOD

In the pentane extraction method of analysis, the sample is accurately weighed, and the bulk volume and gas content are obtained with the mercury pump (see 3.533). The mercury-injected sample is crushed and washed with pentane to remove its oil content. The pentane is evaporated from the oil-pentane mixture by a hot-water bath, and the volume of extracted oil is measured. The oil content, weight, and bulk volume of the core are then known. By using a measured or assumed grain density for the material, a balance can be set up in which the only unknown is water content of the sample. After the water content has been calculated, the gas content, oil content, and water content are added for total pore volume. The average error in oil saturation is ±4 percent of the saturation value, while the average error in water saturation is ±7 percent of the saturation value.

Further details may be found in 5.22 and 5.52.

5.4 GAS-PERMEABILITY DETERMINATION

Permeability of sidewall samples and poorly consolidated cores which can be hand-shaped and mounted in a holder may be measured by the techniques described for conventional core analysis (see 3.4). Extreme caution should be taken to check for cracks, invasion by mud solids, compaction, or rearrangement by sampling and handling, etc. Completely unconsolidated samples must be handled by special techniques which do not apply to routine analysis.

Tests indicate that sidewall samples taken by percussion may increase in permeability through grain fracture, even though porosity may decrease through compaction of the pore spaces. Also, one must guard against possible plugging from mud particles driven into the formation as it is sampled.

Permeability of chips and other fragments have been measured by mercury injection using empirical correlation charts.[13]

5.5 DESCRIPTION OF METHODS FOR ANALYSIS

5.51 RETORT METHOD AT ATMOSPHERIC PRESSURE

(Use of downdraft retort covered by U. S. Patent 2,282,654 and 2,361,844)

5.511 Apparatus

An example of the small sample retort cup is shown in Fig. 5.21F1. A similar cup with an inside diameter of 1⅛ in. should be used for 1-in. diameter samples. These sample-holder cups are used in an electrically heated furnace, of either the single- or multiple-unit type shown in Fig. 3.53F1 and 3.53F2. The condensing tube passes through a water bath, and the recovered liquids are collected in a small, calibrated receiving tube. A volumetric mercury pump is utilized to obtain sample bulk volume and gas content prior to retorting.

5.512 Procedure

Normally, the small sample is divided into two portions, one to be used to determine permeability and the remainder to be weighed and used in determining fluid saturations. This latter portion may vary from 4 to 15 grams. The bulk volume of the unextracted sample is obtained in a volumetric mercury pump. Mercury is then injected into the pore volume occupied by gas or air by increasing the pressure within the mercury pump. The volume of mercury injected at 750 psi to 1,000 psi (depending upon the properties of the sample) is taken as the pore volume occupied by gas or air (see 3.533). The sample containing residual oil, water, and mercury is broken open in the cap of the retort cup to note the type of mercury penetration, and then it is retorted at atmospheric pressure. The retorting procedure is the same as described in 3.532. A drop of demulsifying agent is added to the liquid receiving tube to prevent emulsion formation with the mercury.

5.52 PENTANE EXTRACTION METHOD

5.521 Apparatus

Normal laboratory equipment is suitable for crushing the sample and extracting the oil by decantation. Special glass separator bulbs with a total volume of approximately 100 cc, but with a small, graduated bottom section, are necessary for accurate measurement of the residual oil. A constant-temperature bath is required for the evaporation of the pentane. Fig.

5.52F1 presents an example of a suitable equipment arrangement. A volumetric mercury pump is used to determine sample bulk volume and gas content.

5.522 Procedure

The sample, as received, is divided into two parts, one for extraction and permeability measurement and the other for measurement of porosity and fluid saturations. The bulk volume of the unextracted sample is obtained by displacement in a volumetric mercury pump. The volume of the pore occupied by gas is then determined by the volume of mercury injected at a pressure of about 750 psi to 1,000 psi, as described in 3.533. The sample is removed from the mercury pump, then crushed in a beaker with a small amount of pentane. The pentane is decanted into a separator bulb, and fresh pentane is added to the crushed sample. A total of 50 to 100 cc of pentane is usually sufficient to completely extract the oil. The separator tube is then placed in a constant-temperature bath at 160 F. where the pentane is boiled off. (A straw or similar substance is placed in the tube to facilitate bubble formation and to permit agitation.) The recovered-oil volume is read when no further boiling is observed upon agitation. A lower bath temperature, e.g., 120 F., is desirable when working with high-gravity crudes or distillates.

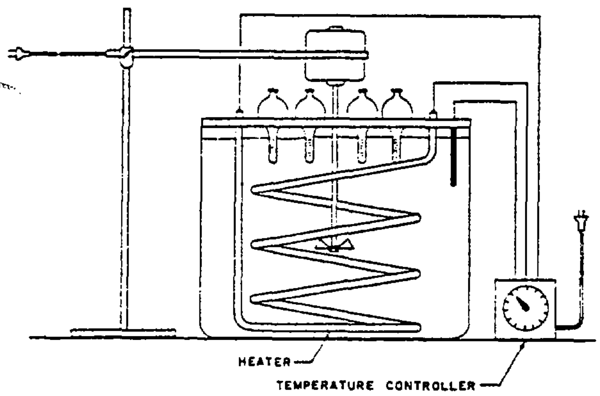


FIG. 5.52F1 — PENTANE EVAPORATION APPARATUS

5.523 Calculations

The volume of recovered oil is corrected for excessive losses with the pentane, or for failure to remove all of the pentane by comparison with calibration curves, as shown in Fig. 5.52F2. The water content is then calculated as a percentage of the bulk volume of the sample by a material-balance equation:

$$\rho n = (1-\phi)\rho_{sd} + V_{bg}\cdot\rho_g + V_{bw}\cdot\rho_w + V_{bo}\cdot\rho_o \quad (24)$$

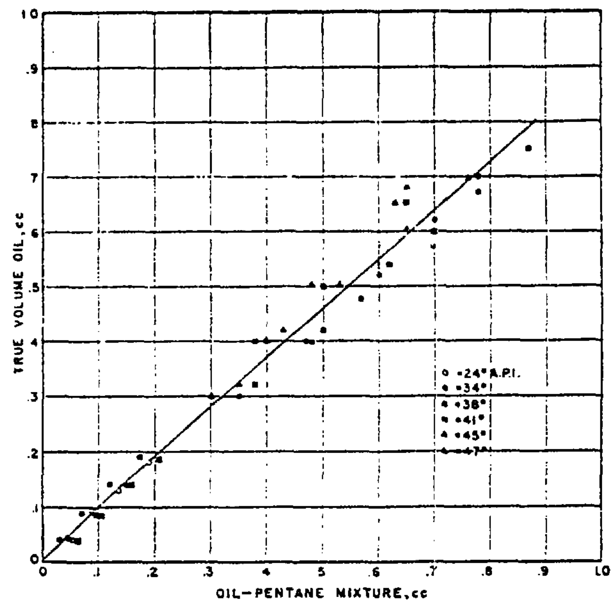


FIG. 5.52F2—PENTANE EVAPORATION DATA WATER-BATH TEMPERATURE, 160 F.

Wherein:

ρn = natural density of the fresh sample.
ϕ = porosity as a fraction of bulk volume.
V_{bg} = gas content as a fraction of bulk volume.
V_{bw} = water content as a fraction of bulk volume.
V_{bo} = oil content as a fraction of bulk volume.
ρ_{sd} = sand grain density.
ρ_g = density, gas.
ρ_w = density, water.
ρ_o = density, oil.

Equation 24 may be rearranged in the form:

$$V_{bw} = [\rho_{sd} - \rho n - V_{bo}(\rho_{sd} - 0.8) - V_{bg}\cdot\rho_{sd}]/(\rho_{sd} - 1) \quad (25)$$

Wherein: 0.8 is taken as the average density of crude oil in the pore spaces and the density of the gas is negligible in comparison with the sand grain density.

The values for V_{bo}, V_{bg}, and ρ_n are measured. The value for ρ_{sd} is either determined experimentally or assumed for a formation where average data are available.

6.0 SUPPLEMENTARY TESTS

The gravity of oil and the salinity of water in core samples are supplementary data often obtained routinely during core analysis. Accordingly, these two tests have been included as the data obtained from them is an aid to interpreting other routine core-analysis data.

6.1 OIL GRAVITY

The specific gravity of the oil must be known in order to convert oil weight to oil volume in the distillation-extraction method for determining fluid saturations (3.55). In the use of the retort method for fluid-saturation measurements, the retorts must be calibrated with crude oils of various gravities (see 3.53 and Fig. 3.53F4). If the gravity of the oil recovered from the retort during the calibration procedure is measured, the gravity change effected by the heating process is obtained. This gravity change varies with the type of oil and geographic source, and the retorts should be calibrated accordingly. If the gravity of the oil recovered from a core sample during a fluid-saturation measurement is determined and the proper gravity-change factor is used, then the gravity of the oil in the core prior to analysis can be estimated.

The oil gravity may be determined by a drop method or a weight method. The drop method consists of suspending a drop of the oil in a liquid medium, the gravity of which can be measured with a hydrometer or a specific-gravity balance. The weight method involves weighing a small amount of the oil in a calibrated pycnometer. The gravity is obtained by dividing the weight of the oil by the pycnometer volume.

6.11 OIL-DROP METHOD

6.111 Apparatus

a. Glass or clear-plastic cylinder.
b. API hydrometers or specific-gravity balance.

6.112 Procedure

A drop of the oil recovered from the core during the fluid-saturation test is placed in a glass or plastic cylinder containing a solution of methyl alcohol and water. The gravity of this solution is subsequently adjusted by the addition of alcohol or water until the oil drop remains suspended; i.e., after gentle agitation of the mixture, the drop neither rises nor falls. The gravity of the solution is then measured with an API hydrometer or a specific-gravity balance. The correct procedure for measuring gravity with a hydrometer is found in *ASTM D 287-55: Method of Test for API Gravity of Petroleum*.[14] The observed API gravity at the test temperature is corrected to the gravity of 60 F. and converted to specific gravity by the use of Tables 5 and 3, respectively, of the *ASTM-IP Petroleum Measurement Tables* (American Edition).[15] A specific-gravity balance permits a direct reading of gravity. A simple chart for converting units of liquid gravity and density may be useful.[16]

6.113 Precautions

a. Any air bubbles adhering to the surface of the oil drop must be removed before adjusting the gravity of the alcohol-water solution.

b. The solution must be gently agitated after each addition of alcohol or water to insure a uniform solution and gravity.

6.114 Advantage

a. Elaborate equipment is not required.

6.115 Limitation

a. Adjustment of alcohol-water ratio is time-consuming.

6.12 WEIGHT METHOD

6.121 Apparatus

a. Balance with accuracy of 0.001 gram.
b. Calibrated pycnometers.

The pycnometers can be made of thin-wall capillary tubing formed in a U-shape. Various sizes can be prepared by varying the length and/or the inside diameter of the tubing. The volumes are calibrated with a liquid of known density (CO_2-free distilled water may be used) with the pycnometer completely full or filled to an etched reference line.

6.122 Procedure

A portion of the oil recovered from the core by the fluid-saturation test is drawn into the pycnometer. It is preferable that the largest practical amount of sample be utilized for the gravity determination. The pycnometer containing the oil is weighed on an analytical balance. The difference between this total oil sample. The gravity is obtained by dividing the weight and the previously determined weight of the pycnometer represents the weight of the oil sample. The gravity is obtained by dividing the weight of the oil by the calibrated volume of the pycnometer.

6.123 Precaution

The pycnometer weight should be held to a minimum. This will reduce errors by allowing the weight of the oil to be a significant amount of the total weight.

6.124 Advantages

a. Extremely accurate readings may be obtained if the pycnometer has been properly calibrated.
d. Determination is made in a short time.

6.2 CORE-WATER SALINITY DETERMINATION

A salinity determination on water present in the core is often desirable as it may aid in core-analysis data interpretation and in electric-log evaluation. Salinity is usually defined as the amount of chloride ion present in the core water expressed as sodium chloride. However, if the salinity is calculated from a resistivity measurement, it represents the contribution from all soluble electrolyte ions, converted to equivalent sodium chloride concentration. Measurements of the core water salinity are based on the assumption that all the soluble electrolytes in the core are contained in the formation water.

If the salinity of the formation water is known, the degree of flushing by the coring fluid may be indicated by the core-water salinity. If the formation-water salinity is unknown, a core-water salinity determination made on low-permeability cores—which are normally less affected by flushing—may approximate the formation-water salinity. At least it represents a lower limit for the salinity of the formation water. The formation-water salinity remains relatively constant within a given reservoir in many areas.

6.21 PREPARATION OF THE SAMPLE AND EXTRACTION OF THE SALT

Approximately 20 grams of sample are selected. The sample may be a portion of that used in previous saturation tests or it may be selected from the core at a point as close as possible to the saturation sample. If the water saturation is not known, it should be measured. The sample, which should be free of contaminants—i.e., coring fluid or other foreign fluids, is ground in a mortar to approximately 16-mesh size and dried in an oven for a period of 1 to 2 hours (3.13). After cooling in a desiccator, the sample is weighed and transferred to a flask. 100 ml of distilled water are added and the mixture is stirred vigorously for several minutes. Agitation is continued periodically for a minimum of 1 hour. The resulting salt solution is filtered or decanted and the chloride content of the water is determined, using either *a*, chemical titration, or *b*, resistivity measurement. The salinity is expressed as parts of sodium chloride per million parts of core water, although other salts are usually present.

6.22 CHEMICAL TITRATION METHOD

6.221 Principle

The filtrate obtained by separation of the crushed sample and the water used in the leaching process is titrated with a standardized silver nitrate solution, using potassium chromate as an indicator. The salinity of the water is expressed as parts per million sodium chloride in the core water.

6.222 Advantages

a. Rapid and convenient method.
b. Chloride determination is accurate.

6.223 Limitations

a. Result is expressed as sodium chloride. Ions other than chlorides present in the solution are not detected.

b. The apparent core-water salinity will be too high if the core contains crystalline salt, which is found in some limestones and dolomites and, to a lesser degree, in some shales.

6.224 Apparatus and Procedure

The apparatus, reagents, and procedure for titration are described in detail in ASTM D 512-55T: Methods of Test for Chloride Ion in Industrial Water.[17] Reference should be made to Referee Method B. The calculation described in this reference will give the salinity in terms of chloride ion instead of sodium chloride. The calculation as sodium chloride is described in 6.24.

6.23 RESISTIVITY MEASUREMENT

6.231 Principle

The total ionic constituents of water may be estimated by measuring the resistivity. The resistivity varies, in an inverse manner, with the ionic concentration of sodium chloride and other salts. Standard graphs, which show the resistivity value for various salinities and temperatures of sodium chloride solutions, can be prepared from data in the literature (Fig. 6.24F1). If the resistivity is known, then the salinity of the core water, expressed as parts per million of sodium chloride, can be determined from such a graph, using a measured resistivity value.

6.232 Advantages

a. Rapid determination.
b. The resistivity data correlate with electric log measurements.
c. Measures total ionic concentration.

6.233 Limitations

a. Resistivity meter and cell must be calibrated.
b. Resistivity value must be corrected to a standard temperature.
c. All ions present in the water are calculated as sodium chloride.
d. The apparent core-water salinity will be greater if the core contains crystalline salt, which is found in some limestones and dolomites and, to a lesser degree, in some shales.

6.234 Apparatus

a. Resistivity cell.
b. Resistivity meter.

6.235 Procedure

The instrumentation should be calibrated with sodium chloride solutions so the measurements check the graphs shown in Fig. 6.24F1. A portion of the solution obtained by leaching the core is placed in the resistivity cell. The resistivity is measured on a suitable meter and calculated in ohm-meters. With the use of a standard graph (Fig. 6.24F1) and suitable calculations (6.24), the resistivity value is converted to a salinity value for the pore water.

Additional details on apparatus and procedure may be found in *ASTM D 1125-50T: Method of Test for Electrical Conductivity for Industrial Water.*[18]

6.24 CALCULATIONS

The measurements from the titration and resistivity methods are calculated to milligrams of sodium chloride leached from the sample. This represents the total salt from the pore water of the sample. The total salt and the amount of pore water obtained by saturation tests are used to calculate the concentration of salt in the pore water and this value is expressed in parts per million of sodium chloride.

a. The normality of the salt solution is calculated from the titration values by the formula:

$$N_1 = ml_2 N_2 / ml_1 \tag{26}$$

Wherein:

N_1 = normality of salt solution titrated.
ml_1 = volume of salt solution titrated.
N_2 = normality of silver nitrate.
ml_2 = volume of silver nitrate used.

The milligrams of sodium chloride leached from the core sample are calculated as follows:

$$N_1 \times 58.5 \times V = \text{total NaCl, mg} \tag{27}$$

Wherein:

V = volume of water, in milliliters, used to leach or extract the sample (6.21).

b. The resistivity value for the salt solution can be converted directly to milligrams of salt from the sample using the conversion chart, Fig. 6.24F1.

c. The volume of the pore water can be obtained directly by difference between the weight of the sample before and after drying if no oil is present. The drying should follow the directions in 3.13.

If the sample contains oil, the fluid saturations (3.2) and the porosity (3.3) must be determined either on this sample or an adjacent piece. The amount of water contained in the sample can be calculated as follows:

$$[(W/D)/(1 - \phi)] = V_b \tag{28}$$

$$(V_b)\ (\phi)\ (S_w) = \text{core water, ml} \tag{29}$$

Wherein:

W = dry weight of sample.
D = grain density.
ϕ = porosity, as fraction.
V_b = bulk volume of sample.
S_w = water saturation, as fraction.

If the grain density has not been determined, use representative value for the formations of interest. The density of water is taken as 1 gram per ml.

d. The salinity of the pore water is obtained by:

$$\frac{\text{mg NaCl (6.24a. or b.)}}{\text{ml pore water (6.24c.)}} \times 100 = \text{mg NaCl/100 g pore water} \tag{30}$$

This value is converted to parts per million using the chart in Fig. 6.24F1.

This chart is designed to be used with the assumptions in 6.2 for core analysis. Values for milligrams per liter obtained by water geo-analysis do not correspond to parts per million in very saline solutions. Thus, the values for milligrams per liter from geo-analysis must be divided by the density of the solution being analyzed to convert to parts per million on this chart.

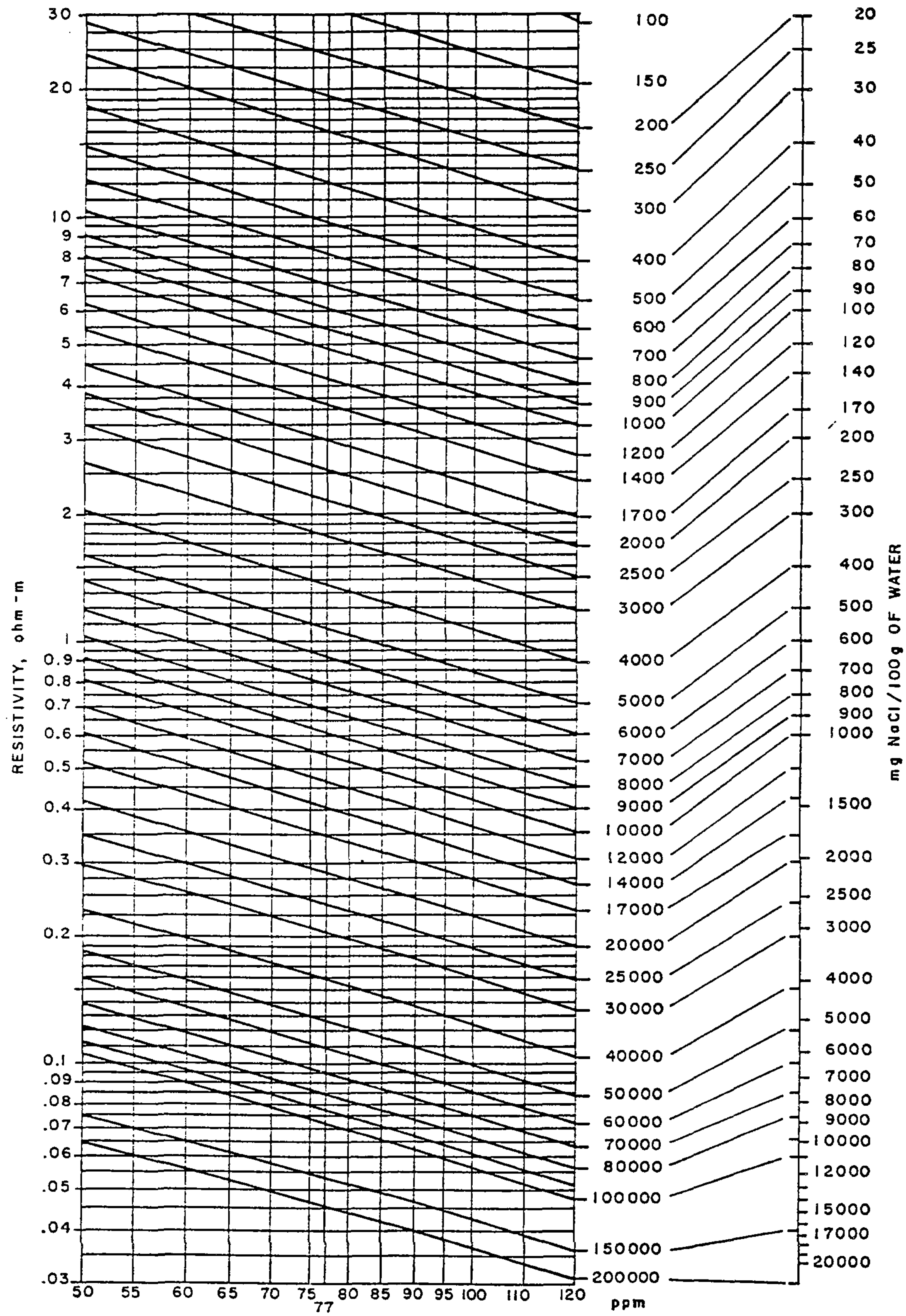


FIG. 6.24F1—CONVERSION CHART FOR SALINITY DETERMINATION
(Data From Critical Tables)

6.25 PRECAUTIONS

6.251 Chemical Titration Method

a. Make blank chloride determination to correct for any chloride present in the glassware and water used in the tests.

b. Standardize silver nitrate solution frequently using a standardized sodium chloride solution.

c. Store silver nitrate solution in brown bottles away from light.

d. An adequate volume of solution must be used so the silver ion used by indicator is negligible compared to the total amount titrated.

e. Proper concentration of indicator should be used.

6.252 *Resistivity Method*

a. Be certain that electrodes of the resistivity cell are clean before making a measurement.

b. Check resistivity meter frequently.

c. Check electrode for cell constant over entire range of use.

d. Correct readings for temperature.

7.0 REPORTING

The major value of the testing program can be lost by inadequate reporting. Core-analysis data are reported in written and graphical form depending upon the type of tests performed and the projected use of the data. These reports become permanent records of the observations made at the time of testing. Furthermore, the value of accurate data for use in reservoir engineering, etc. cannot be over-emphasized. The potential desire to trade or purchase data among operators can place as great a premium on reliable records as any immediate use. Therefore, the more completely and accurately this record is prepared the more valuable it will be at a later time.

7.1 WRITTEN REPORT

The written report should include all of the data, positively identified and tabulated in some convenient form. Identification should include such items as depth, well, geographic location, etc. The exact presentation of the data may be determined between the user and the tester. Reference should be made to the original testing request to provide continuity in the records.

Unusual circumstances should be noted, e.g., core condition, behavior during testing, and anomalies in the data. Any commentary which may assist the interpretation of the data, at present or in the future, should be recorded. The methods used to obtain the core data should be identified. Any deviation from the procedures in the recommended practice should be noted.

7.2 GRAPHICAL REPORT

It is suggested that any standardization of the graphical report forms correspond either to *API RP 31* and *RP 33* for the electrical and nuclear logs, or *RP 34* for hydrocarbon mud logs.

8.0 REFERENCES

[1]Law, J. and Cerini, W. F: A Statistical Approach to Core Analysis Interpretation, *API Drilling and Production Practice*, 373 (1946).

[2]*ASTM Manual on Quality Control Materials, Tech. Pub. 15-C*, Jan. (1951).

[3]Law, J: A Statistical Approach to the Interstitial Heterogeneity of Sand Reservoirs, *Trans. Am. Inst. Mining Met. Engrs. (Petroleum Development and Technology)* **155**, 202 (1944) (reprint, p. 200).

[4]Michell, J. G. and Maher, J. C: Suggested Abbreviations for Lithologic Descriptions, *Am. Assoc. Petroleum Geologists Bull.*, **41**, 2103 (1957).

[5]Conley, F. R. and Burrows, D. B: A Centrifuge Core Cleaner, *J. Petroleum Tech.*, **VIII**, 61, Oct. (1956).

[6]Washburn, E. W. and Bunting, E. N: Determination of Porosity by the Method of Gas Expansion, American Ceramic Society, **5** [48] 112 (1922).

[7]*API RP 27: Recommended Practice for Determining Permeability of Porous Media.* American Petroleum Institute, Dallas, Texas, 3rd Edn., Sept. (1952).

[8]Pirson, S. J: *Elements of Oil Reservoir Engineering*, 22, McGraw-Hill Book Co., Inc., New York, 1950.

[9]Beeson, C. M: The Kobe Porosimeter and the Oil Well Research Porosimeter, *Trans. Am. Inst. Mining Met. Engrs. (Petroleum Development and Technology)* **189**, 313 (1950).

[10]Rall, C. G; Hamontre, H. C; and Taliaferro, D. B: Determination of Porosity by a Bureau of Mines Method, *U. S. Bur. Mines RI 5025*, Feb. (1954).

[11]Calhoun, J. C., Jr: *Fundamentals of Reservoir Engineering*, 83, University of Oklahoma Press, Norman, Okla., 1953.

[12]Collins, R. E: Determination of the Transverse Permeabilities of Large Core Samples from Petroleum Reservoirs, *J. App. Physics*, **23**, 681 (1952).

[13]Burdine, N. T; Gournay, L. S; and Reichertz, P. P. Pore Size Distribution of Reservoir Rocks, *Trans. Am. Inst. Mining Met. Engrs. (Petroleum Development and Technology)* **189**, 195 (1950).

[14]*ASTM D 287-55: Method of Test for API Gravity of Petroleum*, ASTM Standards, Part 5, 156 (1955).

[15]*ASTM-IP Petroleum Measurement Tables* (American Edition); ASTM Designation: D 1250, IP Designation: 200, (1952) or Supplement (1958).

[16]Green, Marvin H: Liquid Gravity and Conversion Chart, *World Oil*, **148** [4] March (1959).

[17]*ASTM D 512-55: Methods of Test for Chloride Ion in Industrial Water*, ASTM Standards, Part 7, 1240 (1955).

[18]*ASTM D 1125-50T: Method of Test for Electrical Conductivity for Industrial Water*, ASTM Standards, Part 7, 1368 (1955).

1.M— 1-76—Johnston
1M— 2-77—Johnston
1.M—12-78—Johnston
1.M—11-80—Johnston
1.M— 6-82—Johnston

TRC *Environmental Solutions Inc.*

APPENDIX B
REVISED SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN
(Rev. 2.0)

Prepared for

United States Environmental Protection Agency

Prepared by

Waste Disposal Inc., Group (WDIG)

Project No. 94-256
November 1997

APPENDIX B
REVISED SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

PAGE NO.

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

APPENDIX B
REVISED SUPPLEMENTAL QUALITY ASSURANCE PROJECT PLAN

B.1 INTRODUCTION

1. This Revised Supplemental Quality Assurance Project Plan (QAPP) has been prepared as Appendix B for the Waste Disposal, Inc. (WDI) Treatability Study Workplan (Treatability Workplan). This Revised Supplemental QAPP outlines the procedures to be used to assure that soil sampling activities provide accurate and representative data. Since this Revised Supplemental QAPP is an appendix to the Treatability Study Workplan (Workplan), project description and organization chapters are not repeated here. The Revised Supplemental Field Sampling and Analysis Plan is included as Appendix A of the Treatability Workplan.

2. Modifications to this QAPP may be required whenever the Treatability Workplan is modified. The primary procedure for making a modification to the Workplan will be through the use of a Technical Memorandum (TM). In the event a modification is required, a TM will be submitted describing the proposed modification and the associated rationale. On approval of the modifications, revised pages, tables or figures as appropriate will be submitted to the EPA.

3. This document is organized in the following sections:
    - B.2 - Project Description
    - B.3 - Project Organization and Responsibility
    - B.4 - Data Quality Objectives
    - B.5 - Sampling Procedures
    - B.6 - Sample Handling and Chain-of-Custody
    - B.7 - Calibration Procedures and Frequency
    - B.8 - Analytical Procedures and Methods
    - B.9 - Data Review, Validation, Verification and Reporting
    - B.10 - Quality Control Checks and Requirements
    - B.11 - Performance and System Audits
    - B.12 - Preventative Maintenance Procedures and Schedules
    - B.13 - Specific Routine Procedures to Assess Quality Assurance Objectives for Measurement Parameters
    - B.14 - Corrective Action
    - B.15 - Quality Assurance Reports to Management
    - B.16 - Documentation and Records Keeping

- B.17 - References
- Attachment B.1 - Quality Assurance/Quality Control Documentation by Selected Contract Laboratory (to be included upon final selection of analytical laboratory)
- Attachment B.2 - Analytical Procedures of Selected Contract Laboratory (to be included upon final selection of analytical laboratory)
- Attachment B.3 - Standard Operating Procedures

B.2 PROJECT DESCRIPTION

1. As is discussed in the Workplan, the objectives of the sampling and analysis are as follows:
    - Soils Activities
        - The objective of soil logging is to confirm the site geologic stratigraphic model and determine source depths.
        - Collect samples for Chemical Analysis for VOCs, SVOCs, pesticides and metals.
        - Collect samples for Geotechnical testing (e.g., moisture, density and permeability).

    The objectives are geared toward completing site characterization necessary for completion of the remedial design.

B.3 PROJECT ORGANIZATION AND RESPONSIBILITY

B.3.1 PROJECT ORGANIZATION

B.3.1.1 Project Management and Team

1. Figure 4.1 of the RD Investigative Activities Workplan illustrates the organization chart for RD activities. The U.S. Environmental Protection Agency (EPA)'s Remedial Project Manager (RPM) for the WDI site, Ms. Andria Benner, will be responsible for managing the project for the EPA and interfacing with the WDIG through the Project Coordinator, Dr. Ian Webster of Unocal. The United States Army Corps of Engineers (COE) will provide Technical Oversight and review of the project for EPA. The RD Investigative Activities, other Response Activities and Closeout Activities will be accomplished by TRC: Dr. Richard Ellison will function as the Principal-in-Charge and Mr. Roberto Puga will act as RD Project Manager to oversee the activities and assure that adequate resources are available to satisfy quality, health and safety, and schedule requirements.

B.3.1.2 Communication and Coordination

1. WDIG will communicate project status to EPA via monthly progress reports as outlined in the Amended Administrative Order, and as indicated in the RD Investigative Activities Workplan.

B.4 DATA QUALITY OBJECTIVES

B.4.1 DATA QUALITY OBJECTIVE DEVELOPMENT

1. The data quality objective (DQO) process is a strategic planning approach based on scientific methods to prepare data collection activities. It is a systematic approach for defining the pertinent criteria for a sampling program including:
   - Where to collect samples.
   - How to collect samples.
   - Tolerable levels of decision errors.
   - How many samples to collect.

   Thereby, the DQO process assures that the type, quantity and quality of environmental data used to evaluate the attainment of the remediation standards are appropriate for the intended use.

2. Additional discussion of DQOs is presented in Section B.4.1 of the RD Investigation Activities Workplan.

B.4.2 DATA QUALITY OBJECTIVES

B.4.2.1 General Data Quality Objectives

1. QA is applied throughout the entire sampling, monitoring, and engineering and design processes to assure that the data collected and engineering and design activities are of known and acceptable quality. Analytical laboratories will be requested to conform with the Contract Laboratory Program Inorganic and Organic Statements of Work in performing the analyses. Measurement procedures will be in accordance with EPA regulations and guidelines. Deviations from approved plans will be documented and justified. Deviations from sampling standard operating procedures (SOPs) will be documented on field logs and the reason for the deviation recorded. Adherence to approved procedures will be verified during system audits.

2. The quality of the measurement data generated will be assessed for precision, accuracy, representativeness, comparability, and completeness (PARCC) based on adherence to the sampling procedures described in the SAP, and available external measures of quality (e.g., standard engineering practice, analysis of trip blanks, duplicates, etc.).

3. The applicable QC procedures and levels of effort in assessing the data quality will be dictated by the intended usage of the data as discussed in Section B.4.1. For laboratory analyses, the quantitative QA goals will be established using the EPA in "Laboratory Documentation Requirements for Data Validation," Document Control No. 9QA-07-90. Methods of analysis will be performed pursuant to standard EPA methods using equivalent contract laboratory program (CLP) protocols and guidelines for QA/QC and data management. Data validation will be expedited by the use of EPA Region IX non-CLP laboratory QC summary forms at the time of submittal. Detection limits, accuracy, precision and completeness requirements will be achieved for those compounds listed in the Record of Decision (ROD) at levels which meet or exceed the DQOs as indicated in Section B.4.3.

B.4.3 SPECIFIC DATA QUALITY OBJECTIVES

1. The DQOs, including detection limits, accuracy, precision and completeness are presented in Table B.1 for each of the analytical methods and media. Section B.13 discusses the methods of calculation for accuracy, precision and completeness. Data from soil analysis will need to achieve Level 3 QA/QC requirements for use in RD activities and risk assessment.

2. The specific contaminants of concern for the WDI site are listed in Table B.1, with their corresponding DQOs for each containment. The required detection limits shown in Table B.1 have been previously discussed with EPA and will, therefore, not be discussed further.

3. Precision of the data is a measure "spread" of the data when more than one measurement is taken of the same sample. Duplicate samples will be collected at a frequency of 10 percent of the samples, or one duplicate per sampling event as indicated in Table B.2. Control limits will be demonstrated by the laboratory and will be included in the reported data. For duplicate measurements, precision will be expressed as the relative percent deviation. Precision requirements are shown in Table B.1.

4. Accuracy is an assessment of the closeness of the measured value to the true value. Accuracy of chemical test results is assessed by spiking samples with known standards and establishing the average recovery. Control limits will be demonstrated by the laboratory as part of the reporting process. For constituent analyses, accuracy is defined in Section B.13. For other

analyses where a quantitative accuracy target is desired, accuracy measurements for the analyses will be carried out at a minimum frequency of either 1 in 20 or 1 per set, whichever is more frequent as indicated in Table B.2.

5. Representativeness is a measure of how closely the results reflect the actual site concentration or distribution of the chemical compounds. Sampling techniques and handling protocols (e.g., storage, preservation, and transportation) have been developed and are discussed in Section B.6 of this document. Proposed documentation will involve the use of field logbooks, sample identification and labeling procedures, and Chain-of-Custody documentation, as indicated throughout this report. These procedures will establish that protocols have been followed and that sample identification and integrity have been assured. Field and transportation blanks and duplicates will be used to assess the potential for field and transport contamination, and method variation. Laboratory sample retrieval, storage and handling procedures will follow standard protocols established by the EPA. Laboratory method blanks will be run at the frequency established by EPA SW-846 laboratory QA protocols.

6. Comparability of the data will be maintained by using EPA defined procedures where available. Section B.8 further describes the analytical procedures. Detection limits for the data obtained will be reported as defined for the specific methods.

7. Completeness is a measure of the amount of valid data obtained from the analytical measurement system. The target completeness objective will be 90 percent; the actual completeness may vary depending on the nature of the samples. The completeness of the data will be assessed during QC reviews.

8. Audits, internal QC checks, preventative maintenance and corrective action, as described herein, will be implemented to maintain QA objectives.

B.5 SAMPLING PROCEDURES

B.5.1 SAMPLE DESIGNATION

B.5.1.1 Project Identification

1. Each sample collected will be identified as having originated from the site by prefacing each sample designation with "WDI," for Waste Disposal, Inc. Each sample will be further designated using "TS" for Treatability Study sample.

B.5.1.2 Sample Location

1. Each sample collected will be identified by an alpha and numerical code, corresponding to the sample media and number, as illustrated below:

B.5.1.3 Sample Identifier

1. Soil samples will have an additional two-digit number as the last component of the sample identifier. This number will correspond to the depth below surface from which the sample was obtained. The following examples represent a treatability soil sample collected at 5 and 10 feet below ground surface (bgs), respectively:
   - WDI-TS-02-05.
   - WDI-TS-02-10.

B.5.1.4 Analytical Parameters, Sample Containers, Methods of Preservation, and Holding Times

1. Information on analytical parameters, sample containers, methods of preservation, and holding times are presented in Table B.1.

B.5.2 SAMPLING METHODS REQUIREMENTS

B.5.2.1 Standard Operating Procedures

1. As previously stated, the QAPP focuses on the use of SOPs. A major function of this QAPP is to provide a library of SOPs that are generally applicable to QA/QC activities. Relevant SOPs are located in Appendix B.3 of the Revised QAPP for the RD Investigative Activities Workplan.

2. Sampling and sample custody procedures are described in the Revised Supplemental QAPP.

3. The SOPs will be comprehensive in that they will include a list of the equipment and detailed procedures necessary for performing the activity. The SOPs will reference, as appropriate, relevant information provided in other SOPs, and the General Workplan, SAP, QAPP and HSP rather than repeating such information in the SOP. This will help to maintain consistency among the procedures used.

B.5.2.2 Sampling and Field Procedures

1. Chapter 2 of the Treatability Study Workplan describes the anticipated activities to fulfill the requirements of the Scope of Work (SOW). The Revised Supplemental SAP describes the actual sampling, analysis, monitoring and measurement procedures presently planned and discussed in the Workplan. Sampling rationale and sample site selection are also discussed in the Revised Supplemental FSAP. This section of the Revised Supplement QAPP discusses the QA aspects and requirements of those procedures.

2. The following subsections for the individual procedures contain field QA/QC requirements for assuring quality data collection. Procedures for calibration of instruments used during field activities are included in Section B.7. Chain-of-Custody procedures are described in Section B.6 and in SOP I.

3. The sampling and field procedures described in this section will result in the generation of residual materials (e.g., soil cuttings, ground water). These materials will be handled and disposed of as described in Section A.5.3 of the FSAP.

B.5.2.3 Sampling Procedures

B.5.2.3.1 Soil Sampling Procedures

1. The following sampling procedures will be used during the soil sampling activities:
   - Retrieval of soil samples using a hydraulically pushed boring.
   - Selection of representative soil sample by visual inspection through the acrylic tube.
   - Collection and field extraction of sample using EPA method 5035 (SOP O).
   - Shipment of samples to the laboratory.
   - Analysis of samples using EPA method 5035 of VOCs.

2. The following QA/QC procedures as provided in SOP O will be followed for handling soil samples:

3. Other QA/QC procedures include the assurance that the proper soil samples are identified for analysis. The field team leader will check the sampling notebook and Chain-of-Custody records versus the actual sample shipment container prior to shipment.

B.5.3 FIELD MEASUREMENTS

B.5.3.1 Borehole Logging

1. A log will be maintained to characterize the soils encountered during soil sampling. The major components to be recorded in the log by the onsite field geologist, working under the supervision of a California Registered Professional Geologist, or Geotechnical Engineer, working under the supervision of a California Registered Professional Geotechnical Engineer, includes the following:
   - Description:
     - The depth, color and texture of cuttings; percentage of gravel, sand silt and clay; descriptive comments including odor and indications of potential contamination (e.g., staining); and moisture content noted from grab or split-barrel samples. These soil properties will be reported using the Unified Soil Classification System (USCS).
     - An identification of each sample retained in a sample bag or stainless steel sleeve, including borehole number and depth, for future cross-reference.
     - When obtaining samples with a split-barrel sampler, blow counts will be recorded for every 0.5-foot penetration (i.e., three blow counts per 1.5-foot sampler), with a specified weight falling a specified and consistent distance.
   - Headspace Analysis:
     - For the California split-spoon sampler, half of the soil volume in the middle or bottom stainless steel sleeve will be removed and placed inside a small resealable plastic bag.
     - For the Hydraulically Pushed Borings, material from either end of the 3-foot clear polyacrylate sleeve will be removed from the sampler as described above.
     - For either sampling procedure, the sleeves or bags will be left in the sunlight for approximately 15 to 30 minutes, after which time the headspace will be analyzed using an Flame Ionization Detector (FID) to measure potential volatile contamination.

2. QA/QC of the boring logs consists of the following activities performed by the field team leader:
   - Consistency of the material description across boreholes, if similar materials are encountered.
   - Checking to see that the log accurately identifies the retained samples (e.g., cross-check versus stored and shipped samples).
   - Assure that the log has necessary descriptive and identifying information.

B.5.3.2 Field Parameters

B.5.3.2.1 Soils

1. Soil samples will be evaluated for visible degradation and volatile hydrocarbons as part of routine screening by the onsite geologist/engineer, as discussed below.

   - Visible Degradation: The drill cuttings will be observed for the presence of visible staining, color, moisture or odors. The observations will be recorded on Field Boring Logs (SOP J).

2. QA/QC procedures include checking for consistency in soil and hydrocarbon descriptions and assuring appropriate instrument calibration.

B.6 SAMPLE HANDLING AND CHAIN-OF-CUTODY RECORDS

B.6.1 CHAIN-OF-CUSTODY RECORDS

1. A Chain-of-Custody record will be used as physical evidence to document sample custody. The Chain-of-Custody record provides the means to identify, track, and monitor each individual sample from the point of collection through final data reporting. A Chain-of-Custody record will be required for each shipment of samples. Detail description of the Chain-of-Custody procedure is provided in Appendix B of the RD Investigative Activities Workplan and SOP I.

B.6.2 SAMPLE HANDLING

B.6.2.1 Sample Containers

1. Sample containers will meet or exceed EPA Level 3 requirements and will be certified clean by the supplier prior to use. Sample container types are specified in Table B.1 for each type of analysis requested.

2. Sampling kits will be provided to the field team leader by the laboratory. The project manager will be responsible for ordering sampling kits for the duration of the project. Sampling kits will be shipped directly to TRC in Irvine, California prior to the start of each sampling phase. Additional sampling kits may also be required during the period of sampling.

3. Upon arrival, designated personnel will check each shipment to verify that the correct number and type of containers have been shipped and received. The sample custodian will be notified if discrepancies exist between the sample shipment and sample order. The sampling kits will be enclosed in coolers, and will include the appropriate sample containers, Chain-of-Custody

record forms, and appropriate shipping blanks and field blanks (supply of reagent water). Completed sampling kits will be returned to the sample custodian by the field sampler after the samples have been collected.

4. Each sample container will be individually labeled. Clear plastic tape will be placed over each completed label to protect it from damage.

5. The field team leader will assure that each box of sample containers has its appropriate certificate from the supplier.

B.6.2.2 Sample Preservation

1. Sample preservation requirements are specified in Table B.1 for each type of analysis requested, and media.

2. The field team leader will assure that the appropriate equipment for sample preservation is available in the field and that proper documentation of their use has been made in the field sampling logbook.

B.6.2.3 Sample Shipment

1. Samples will be packed in the following manner for shipment as provided in SOP H and in Appendix B of the RD Investigative Activities Workplan:

2. The field team leader will check each sample shipment to assure proper labeling, packaging and documentation.

B.6.2.4 Sample Designation

1. As outlined in the Workplan, the primary purpose of the field investigation activities is to supplement Remedial Investigation activities and prior Predesign field activities to complete the Remedial Design.

2. The sampling efforts to be used in support of the collection of soil samples will incorporate the following strategies:

- Follow appropriate protocols in the Health and Safety Plan to minimize exposure to potentially contaminated media.
- Follow labeling protocols for each sample collected. Detailed protocols are provided in the Revised Supplemental QAPP Section B.6.2.
- Place samples in laboratory-certified clean receptacles.
- Adhere to field sample collection and handling procedures as described herein, and supported by QC measures outlined in the QAPP (Appendix B of the RD Investigative Workplan).
- Follow sample packaging and Chain-of-Custody protocols to assure that samples which may be analyzed are delivered to the laboratory and stored appropriately. Detailed protocols are provided in the RD Investigative Activities Workplan Section B.6.1.

3. EPA will be notified not less than 14 days in advance of any sample collection activity.

B.7 CALIBRATION PROCEDURES AND FREQUENCY

B.7.1 FIELD CALIBRATION PROCEDURES

1. Field equipment requiring calibration includes portable volatile organic compounds (VOC) monitoring equipment such as the FID analysis, are provided in Appendix B of the RD Investigative Activities Workplan.

B.7.2 LABORATORY CALIBRATION PROCEDURES

1. Calibration procedures will be as defined in EPA standard methods. For analysis of soil gas samples, the required calibrations will be performed in accordance with EPA established methods. Analyses calibrations for ground water and soil gas will be performed as discussed below. Specific calibration procedures will be incorporated into this document as part of the selected laboratories' QA/QC documentation. Details on the laboratory calibration procedure is provided in Section B.7.2 of the RD Investigative Activities Workplan.

B.8 ANALYTICAL PROCEDURES AND METHODS

1. A summary of the analytical procedures for subsurface soil samples, the analytical QA control limits, and the detection limits to be used for the listed parameters, are presented in Table B.1. The specific laboratory procedures will be included as Attachment B.2 once a laboratory is selected.

2. Analyses for VOCs, SVOCs, pesticides and metals will be conducted pursuant to Contract Laboratory Program requirements, including detection limits, accuracy, precision, surrogate recoveries, duplicate samples and matrix spikes as indicated in Table B.3. For purposes of this QAPP, the Contract Laboratory Program requirements have been incorporated by reference.

3. To achieve the detection limits required for this project, the selected laboratory will demonstrate analytical capabilities with historical and ongoing minimum detection limit (MDL) studies. Documentation will be provided to support the quality of the data that is reported.

4. The minimum QA/QC deliverables for soil gas and ground water analyses are indicated as follows:
   - Case Narrative
   - Sample Analysis Receipt
   - Sample Cross Reference (if required)
   - Chain-of-Custody Records
   - Analysis Report
     - Preparation and Analysis Run Logs
     - Raw Data and Chromatograms
   - QC Summary
     - Minimum Detection Limit Summary
     - Initial Calibration Data
     - Detailed QA/QC Data
     - Corrective Action Reports

   Once a laboratory is selected, representative examples of the QA/QC documentation will be provided in Attachment B.1. Table B.4 provides the Level 3 laboratory documentation requirements from the laboratory.

B.8.1 SOIL SAMPLE ANALYTICAL PROCEDURES

1. Table B.1 lists the specific analyses and EPA methods for the soil sampling investigation, as well as the analytical holding times and sample volumes associated with these methods. Complete Chain-of-Custody documentation will be initiated in the field, and will accompany the samples to the analytical laboratory. Laboratory QA/QC procedures will be equivalent to those required by EPA-Contract Laboratory Program (CLP) laboratories, and will conform with these requirements.

B.9 DATA REVIEW, VALIDATION, VERIFICATION AND REPORTING

1. The first level of review and consequent data reduction, validation and reporting is done at the laboratory. Data reduction, validation and reporting at the laboratory will be implemented in accordance with standard EPA methods for analytical and QA protocols. In general, the laboratory reviews will be performed by the laboratory analyst, the QA officer and laboratory management pursuant to the procedures summarized in Sections B.6 and B.7. Additional details are provided in Section B.9 of the RD Investigative Activities Workplan.

B.10 QUALITY CONTROL CHECKS AND REQUIREMENTS

B.10.1 SOIL SAMPLE QUALITY CONTROL

1. Table B.8 outlines the basic field QC requirements for soil samples. Soil sampling requires trip blanks (only for VOCs), equipment rinsates, and field duplicates. The following information defines and explains the required field QC samples.
   - Trip Blanks - Trip blanks are analyte-free methanol taken from the laboratory to the sampling site and returned to the laboratory with the VOC samples. One trip blank will accompany each cooler containing VOC samples. Each will be stored at the laboratory with the samples and analyzed by the laboratory. Trip blanks will be analyzed only for VOC's.
   - Equipment Rinsates - Equipment rinsates are the final, analyte-free water rinse from equipment cleaning. If equipment rinsates are generated, they will be collected daily during a sample event. Initially, only samples collected every other day will be analyzed. If analytes pertinent to the project are found in the rinsate, the remaining samples will be analyzed. The results from the blanks will be used to flag or assess the levels of analytes in the samples. This comparison is made during data validation. The rinsates will be analyzed for the same parameters as the related samples. Equipment rinsate samples will be collected from sampling equipment such as reusable Teflon® and stainless steel bailers and trowels.
   - Field Duplicates/Splits - The duplicates for soil samples will be collected simultaneously. Field duplicates will be collected at a frequency of 10 percent of the total number of sampling points. Duplicates will be sent to the primary laboratory for analysis.

B.10.2 LABORATORY QUALITY CONTROL PROCEDURES

1. Laboratory QC procedures will be consistent with EPA Level 3 QC guidelines, as indicated in the CLP Program. The QA/QC Plan for the subcontracted laboratory (to be selected), will be provided in Attachment B.1 of this document.

2. Laboratory QC procedures will include the following:
   - Instrument calibrations and standards as defined in Section B.7.
   - Analytical methodology according to methods defined in Tables B.2 and B.3.
   - Laboratory blank measurements will be performed at a minimum of 1 per day or 1 per 20 samples.
   - Data reduction and reporting will proceed as described in Section B.8.
   - Accuracy and precision measurements will be performed as defined in Section B.13, at a minimum of 1 in 20, or 1 per sample group.
   - A minimum of one laboratory control sample will be analyzed with each sample run.

3. The laboratory will report all results, even those below established action levels when feasible.

B.11 PERFORMANCE AND SYSTEM AUDITS

B.11.1 PERFORMANCE AUDITS

1. The project manager will monitor and audit the performance of the QA procedures. Audits may be scheduled to evaluate the execution of sample identification, sample control, Chain-of-Custody procedures, field notebooks, sampling procedures and field measurements.

2. The field activities manager will review work product quality to evaluate whether the project is performed in accordance with approved QA procedures.

3. The project manager will request confirmation of audits performed by personnel from the selected laboratory in accordance with the QA/QC documentation provided in Attachment B.1.

4. The project manager will coordinate the activities of the review team.

B.11.2 FIELD AUDITS

1. Additional discussion of field audits is provided in Section B.11.2 of the RD Investigative Activities Workplan.

B.11.3 LABORATORY AUDITS

1. Laboratory audits will be performed by laboratories internal staff in a similar fashion as field audits using a checklist to be developed and included in Attachment B.1. A discussion of laboratory audits is provided in Section B.11.3 of the RD Investigative Activities Workplan.

B.12 PREVENTATIVE MAINTENANCE PROCEDURES AND SCHEDULES

1. Instrument maintenance logbooks are maintained in the laboratory at all times. The logbooks generally contain a schedule of maintenance, as well as a complete history of past maintenance, both routine and nonroutine. A discussion of Preventative Maintenance Procedures and Schedules is provided in Section B.12 of the RD Investigative Activities Workplan.

B.13 SPECIFIC ROUTINE PROCEDURES TO ASSESS QUALITY ASSURANCE OBJECTIVES MEASUREMENT PARAMETERS

1. Data assessment will follow the in-depth data review and validation procedures described in Section B.8. Section B.13 and B.8 of the RD Investigative Activities Workplan provides a detailed discussion of Procedures to Assess Quality Assurance Measurement Parameters.

B.14 CORRECTIVE ACTION

1. Whenever quality deficiencies for field or laboratory activities are observed that warrant management attention, the QA officer will issue a formal corrective action request, with multicopy forms to the project manager. The project manager will complete the form and sign it when corrective action has been implemented. The original will be returned to the QA officer "to close the loop." The QA officer maintains a record of corrective action requests. A detailed discussion of Corrective Actions is provided in Section B.14 of the RD Investigative Activities Workplan.

B.15 QUALITY ASSURANCE REPORTS TO MANAGEMENT

1. The Project Manager may request that a report be made on the performance of sample collection and data quality, calculations or drawings. The report may include:
   - Assessment of measurement data accuracy, precision and completeness.
   - Results of performance audits.
   - Results of systems audits.
   - Identification of significant QA problems and recommended solutions.

2. Alternatively, in lieu of a separate QA Report, sampling and field measurement data quality information may be summarized and included with the raw data as appropriate.

3. TRC (Project Manager) will prepare and issue a QA summary report within 30 days of the completion of a sampling event.

B.16 DOCUMENTATION AND RECORDS KEEPING

1. Documentation and records keeping will be performed as indicated in SOP N and in Section B.16 of the RD Investigative Activities Workplan. These document control procedures apply to project documents that specify quality requirements or prescribe how project activities affecting quality will be conducted.

B.17 REFERENCES

EPA Order 5360.1. *Policy and Program Requirements to Implement the Mandatory Quality Assurance Program*, U.S. Environmental Protection Agency, Washington, DC (April 1984).

48 CFR Chapter 15, Subpart 1546.2, "Contract Quality Requirements."

ISO 8402-1994, *Quality Management and Quality Assurance - Vocabulary* (April 1994).

QAMS-005/80, *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*, U.S. EPA (December 1980).

Guidance for the Data Quality Objectives Process, EPA QA/G-4, U.S. EPA (August 1994).

EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations. EPA QA/R-5. U.S. EPA 1994 Draft Final.

EPA Requirements for Quality Management Plans. EPA QA/R-2. August 1994.

Quality Management Program Plan for Region 10 RQMP - 001/96.

TABLE B.1

SOIL ANALYSES AND QUALITY CONTROL OBJECTIVES
WASTE DISPOSAL, INC.

PARAMETERS	ANALYTICAL PROCEDURE (EPA METHOD NO.)	LABORATORY SPECIFIC MEASUREMENT QUALITY OBJECTIVES (MQOs)				TYPE OF CONTAINER	PRESERVATIVE	ANALYTICAL HOLDING TIMES	REMARKS
		Detection Limit (µg/Kg)	Accuracy[1] (%)	Precision[2] (%)	Completeness (%)				
METALS									
• Aluminum	6010A	10.0	80 - 120	±30	90	1- To 8-Ounce Amber Jar or Tube	None, Cool to 4°C	6 Months	
• Antimony	6010A	10,000	80 - 120	±30	90				
• Arsenic	7060	5,000	80 - 120	±30	90				
• Barium	6010A	500	80 - 120	±30	90				
• Beryllium	6010A	100	80 - 120	±30	90				
• Cadmium	6010A	1,000	80 - 120	±30	90				
• Calcium	6010A	50,000	80 - 120	±30	90				
• Cobalt	6010A	4,000	80 - 120	±30	90				
• Chromium	6010A	1,000	80 - 120	±30	90				
• Iron	6010A	4,000	80 - 120	±30	90				
• Lead	6010A	5,000	80 - 120	±30	90				
• Magnesium	7421	200	80 - 120	±30	90				
• Manganese	6010A	1,000	80 - 120	±30	90				
• Mercury	7471	100	83 - 124	±30	90				
• Nickel	7470	4,000	80 - 120	±30	90				
• Selenium	6010A	10,000	80 - 120	±30	90				
• Sodium	6010A	200	80 - 120	±30	90				
• Thallium	7740	7,000	80 - 120	±30	90				
• Vanadium	6010A	4,000	80 - 120	±30	90				
• Zinc	6010A	1,000	80 - 120	±30	90				
VOLATILE ORGANIC COMPOUNDS (VOCs)									
• 1,1,1-Trichloroethane	5035	5.0	70 - 135	±30	90	Two 40-mL VOA Vials with Stir Bars and Septum Heads	Sodium Bisulfate and 10 mL Methanol	14 Days	Sampling Using EPA Method 5035
• 1,1,2,2-Tetrachloroethane	5035	5.0	71 - 105	±30	90				
• 1,1,2-Trichloroethane	5035	5.0	70 - 135	±30	90				
• 1,1-Dichloroethane	5035	5.0	68 - 133	±30	90				
• 1,1-Dichloroethene	5035	5.0	58 - 131	±30	90				
• 1,2-Dichloroethane	5035	5.0	85 - 108	±30	90				
• 1,2-Dichloropropane	5035	5.0	62 - 130	±30	90				
• 2-Butanone	5035	10	48 - 140	±30	90				
• 2-Chloroethyl Vinyl Ether	5035	10	65 - 121	±30	90				
• 2-Hexanone	5035	50	23 - 166	±30	90				
• 4-Methyl-2pentanone	5035	10	40 - 135	±30	90				
• Acetone	5035	5	62 - 148	±30	90				
• Benzene	5035	5	76 - 123	±30	90				
• Bromodichloromethane	5035	5	65 - 148	±30	90				
• Bromoform	5035	5	75 - 135	±30	90				
• Bromomethane	5035	5	67 - 129	±30	90				
• Carbon Disulfide	5035	20	32 - 180	±30	90				
• Carbon Tetrachloride	5035	5	70 - 140	±30	90				
• Chloroethane	5035	5	54 - 135	±30	90				
• Chloroform	5035	5	70 - 125	±30	90				
• Chloromethane	5035	5	40 - 136	±30	90				
• cis-1,3-Dichloropropene	5035	5	67 - 130	±30	90				
• 1,2, Dibromoethane	5035	5	64 - 140	±30	90				
• Methylene Chloride	5035	5	60 - 126	±30	90				

(1) Based on Matrix Spike Percent Recovery.
(2) Based on Duplicate Samples.

TABLE B.1

SOIL ANALYSES AND QUALITY CONTROL OBJECTIVES
WASTE DISPOSAL, INC.
(Continued)

PARAMETERS	ANALYTICAL PROCEDURE (EPA METHOD NO.)	LABORATORY SPECIFIC MEASUREMENT QUALITY OBJECTIVES (MQOs)				TYPE OF CONTAINER	PRESERVATIVE	ANALYTICAL HOLDING TIMES	REMARKS
		Detection Limit (µg/Kg)	Accuracy(1) (%)	Precision(2) (%)	Completeness (%)				
VOLATILE ORGANIC COMPOUNDS (VOCs) (Continud)									
• Tetrachloroethene	5035	5	69 - 148	±30	90				
• trans-1,2-Dichloroethee	5035	5	67 - 130	±30	90				
• trans-1,3-Dichloropropene	5035	5	70 - 127	±30	90				
• Trichloroethene	5035	5	71 - 157	±30	90				
• Vinyl Acetate	5035	5	29 - 146	±30	90				
• Vinyl Chloride	5035	5	57 - 133	±30	90				
SVOCS									
• Acenaphthene	8270	200	56 - 136	±30	90	1- to 8-Ounce Amber Jar or Tube	None, Cool to 4°C	7 Days to Extract; 40 Days After Extraction	
• Acenaphylene	8270	200	57 - 127	±30	90				
• Anthracene	8270	200	57 - 125	±30	90				
• Benzo(a)anthracene	8270	200	44 - 138	±30	90				
• Benzo(b)fluoranthene	8270	200	24 - 131	±30	90				
• Benzo(k)fluoranthene	8270	200	39 - 142	±30	90				
• Benzo(g,h,i)perylene	8270	200	25 - 157	±30	90				
• Benzo(a)pyrene	8270	200	34 - 128	±30	90				
• bis(2-Chloroethyl)ether	8270	200	49 - 111	±30	90				
• bis(2-Chloroisopropyl)ether	8270	200	38 - 147	±30	90				
• bis(2-Ethylhexyl)phthalate	8270	400	41 - 147	±30	90				
• 4-Bromophenyl-phenylether	8270	200	59 - 122	±30	90				
• Butylbenzylphthalate	8270	200	37 - 151	±30	90				
• 4-Chloroaniline	8270	200	27 - 120	±30	90				
• 4-Chloro-3-methylphenol	8270	200	55 - 131	±30	90				
• 2-Chloronaphthalene	8270	200	37 - 102	±30	90				
• 4-Chlorophenyl-phenylether	8270	200	59 - 124	±30	90				
• Chrysene	8270	200	43 - 147	±30	90				
• Dibenz(a,h)anthracene	8270	200	30 - 154	±30	90				
• Dibenz(a,h)acridine	8270	200	58 - 128	±30	90				
• Dibenzofuran	8270	200	54 - 128	±30	90				
• Di-n-butylphthalate	8270	200	53 - 125	±30	90				
• 1,2-Dichlorobenzene	8270	200	48 - 112	±30	90				
• 1,3-Dichlorobenzene	8270	200	48 - 112	±30	90				
• 1,4-Dichlorobenzene	8270	200	48 - 112	±30	90				
• 3,3-Dichlorobenzidine	8270	200	40 - 135	±30	90				
• 2,4-Dichlorophenol	8270	200	49 - 116	±30	90				
• Dimethylphthalate	8270	200	61 - 129	±30	90				
• 4,6-Dinitro-2-methylphenol	8270	200	46 - 139	±30	90				
• 2,4-Dinitrophenol	8270	200	48 - 135	±30	90				
• 2,4-Dinitrotoluene	8270	200	44 - 128	±30	90				
• 2,6-Dinitrotoluene	8270	200	48 - 130	±30	90				
• Di-n-octylphthalate	8270	200	44 - 138	±30	90				
• Fluoranthene	8270	200	39 - 137	±30	90				
• Fluorene	8270	200	39 - 137	±30	90				
• Indeno(1,2,3-ad)pyrene	8270	200	25 - 162	±30	90				
• Isophorone	8270	200	40 - 120	±30	90				
• 2-Methylnaphthalene	8270	200	5 - 165	±30	90				
• 2-Methylphenol	8270	200	60 - 135	±30	90				
• 4-Methylphenol	8270	200	48 - 141	±30	90				

(1) Based on Matrix Spike Percent Recovery.
(2) Based on Duplicate Samples.

TABLE B.1

SOIL ANALYSES AND QUALITY CONTROL OBJECTIVES
WASTE DISPOSAL, INC.
(Continued)

PARAMETERS	ANALYTICAL PROCEDURE (EPA METHOD NO.)	LABORATORY SPECIFIC MEASUREMENT QUALITY OBJECTIVES (MQOs)				TYPE OF CONTAINER	PRESERVATIVE	ANALYTICAL HOLDING TIMES	REMARKS
		Detection Limit (μg/Kg)	Accuracy(1) (%)	Precision(2) (%)	Completeness (%)				
SVOCS (Continued)									
• 2-Nitroaniline	8270	200	59 - 129	±30	90				
• 4-Nitroaniline	8270	400	29 - 171	±30	90				
• 2-Nitrophenol	8270	200	48 - 114	±30	90				
• N-Nitrosophenylamine	8270	200	43 - 92	±30	90				
• N-Nitroso-di-n-propylanine	8270	200	32 - 137	±30	90				
• Naphthalene	8270	200	49 - 106	±30	90				
• Nitrobenzene	8270	200	50 - 114	±30	90				
• Pentachlorophenol	8270	400	39 - 157	±30	90				
• Phenanthrene	8270	200	61 - 122	±30	90				
• Phenol	8270	200	43 - 119	±30	90				
• Pyrene	8270	200	52 - 149	±30	90				
• 1,2,4-Trichlorobenzene	8270	200	48 - 114	±30	90				
• 2,4,5-Trichlorophenol	8270	200	54 - 131	±30	90				
• 2,4,6-Trichlorophenol	8270	200	56 - 136	±30	90				
PESTICIDES/PCBs(3)									
• 4,4'-DDD	8080	1	56 - 151	±30	90	1- 8-Ounce Amber Jar or Tube	None, Cool to 4°C	14 Days to Extract; 40 Days After Extraction	
• 4,4'-DDE	8080	1	70 - 136	±30	90				
• 4,4'-DDT	8080	1	51 - 155	±30	90				
• Aldrin	8080	2	68 - 138	±30	90				
• Alpha-BHC	8080	2	64 - 135	±30	90				
• Beta-BHC	8080	0.7	69 - 140	±30	90				
• Delta-BHC	8080	2	74 - 137	±30	90				
• Gamma-BHC	8080	1	71 - 131	±30	90				
• Chlordane	8080	30	20 - 160	±30	90				
• Dieldrin	8080	1	68 - 138	±30	90				
• Endosulfan I	8080	2	28 - 148	±30	90				
• Endosulfan II	8080	1	41 - 137	±30	90				
• Endosulfan Sulfate	8080	2	36 - 159	±30	90				
• Endrin	8080	1	53 - 167	±30	90				
• Endrin Aldehyde	8080	1	48 - 140	±30	90				
• Endrin Ketone	8080	1	40 - 150	±30	90				
• Heptachlor	8080	1	68 - 152	±30	90				
• Heptachlorepoxide	8080	3	73 - 138	±30	90				
• Methoxychlor	8080	1	8 - 182	±30	90				
• Toxaphene	8080	100	20 - 160	±30	90				
• PCBs	8080	100	65 - 134	±30	90				
PETROLEUM HYDROCARBONS									
• C:8 - C:44	ASTM D-2887	10,000	40 - 140	±30	90	1 - 8-Ounce Amber Jar or Tube	None, Cool to 4°C	14 Days to Extract; 40 Days After Extraction	

94-256/Rpts/RdlnAcWo/Rev.2.0 (11/17/97/mc)

(1) Based on Matrix Spike Percent Recovery.
(2) Based on Duplicate Samples.
(3) Ground water samples will not be analyzed for pesticides/PCBs.

TABLE B.2

FIELD COLLECTION QUALITY ASSURANCE REQUIREMENTS
WASTE DISPOSAL, INC.

ANALYSIS	TRIP BLANK	FIELD BLANK(1)	FIELD DUPLICATE(2)	MATRIX SPIKE AND MATRIX SPIKE DUPLICATES(3)
Soil Samples				
Organics(4)	1 per 20 samples or 1 per sample shipment, whichever is greater	N/A	1 per 10 samples or 1 per sample shipment, whichever is greater	1 per 20 samples or 1 per sample shipment, whichever is greater
Inorganics(5)	None	N/A	1 per 10 samples or 1 per sample shipment, whichever is greater	1 per 20 samples or 1 per sample shipment, whichever is greater

94-256 (Rpts/RdInAcWo/Rev1.0/AppB)(11/17/97/mc)

(1) Field blanks are not required for soil samples.
(2) Field duplicates require an additional sample volume (see Table B.1). Note that field duplicates will be labeled so the laboratory cannot determine that the sample is a field duplicate. Field duplicates will be collected as split samples from the actual sample collected.
(3) MS/MSD samples require two additional sample volumes for organic analysis. Matrix spike samples require an additional sample volume for inorganic analyses (see Table B.1).
(4) Includes VOCs, SVOCs and pesticides/PCBs and Petroleum Hydrocarbons.
(5) Includes metals.

TABLE B.3

LABORATORY QUALITY ASSURANCE REQUIREMENTS
SOIL AND SUMP MATERIAL ANALYSES
WASTE DISPOSAL, INC.

PARAMETER GROUP	CALIBRATION METHOD	CALIBRATION/QC SAMPLING FREQUENCY	ACCEPTANCE CRITERIA
Metals (Method 6010A, 7062, 7421, 7470, 7740)	Calibration Curve	At start of analysis or when continuing calibration verification standard is out of control.	Per instrument operating manual
	Initial Calibration Verification Standard	After calibration and before sample analysis	±10 percent of true value
	Calibration Blank	Every 10 samples	<Method reporting limit
	Continuing Calibration Verification Standard	Every 10 samples	±10 percent of expected value
	Instrument Blank	1 every 10 samples	<Method reporting limit
	Method Blank	1 every 20 samples	<Method reporting limit
	Laboratory Duplicate	1 every 20 samples	Precision (%) See Table B.1 Accuracy (%) See Table B.1 Completeness (%) See Table B.1
	MS/MSD	1 every 20 samples	80 to 120 percent recovery
	Laboratory Control Sample	1 every 20 samples	80 to 120 percent recovery
Volatile Organic Compounds (Method 5035)	Calibration Curve	At start of analysis or when continuing calibration verification standard is out of control	20 percent relative standard deviation if average response factor is used.
	Initial Calibration Verification Standard	After calibration and before sample analysis	±15 percent of true value
	Calibration Blank	Every 10 samples	<Method reporting limit
	Continuing Calibration Verification Standard	Every 10 samples	±15 percent of true value
	Instrument Blank	1 every 10 samples	<Method reporting limit
	Method Blank	1 every 20 samples	<Method reporting limit
	MS/MSD and LCS	1 every 20 samples	Precision (%) 30 RPD Accuracy (%) 50 to 125 percent recovery Completeness (%) 90 percent recovery
	Surrogate Compound	Every sample	4-bromofluorobenzene 86 to 115 percent recovery α, α, α-trifluorotoluene 86 to 115 percent recovery Dibromofluoromethane 86 to 115 percent recovery

NOTE: MS = Matrix Spike; MSD = Matrix Spike Duplicate; LCS = Laboratory Control Sample.
RPD = Relative Percent Difference.

TABLE B.3

LABORATORY QUALITY ASSURANCE REQUIREMENTS
SOIL AND SUMP MATERIAL ANALYSES
WASTE DISPOSAL, INC.
(Continued)

PARAMETER GROUP	CALIBRATION METHOD	CALIBRATION/QC SAMPLING FREQUENCY	ACCEPTANCE CRITERIA
Semivolatile Organic Compounds (Method 8270)	Calibration Curve (5 point)	At start of analysis or when continuing calibration verification standard is out of control	Per method
	Initial Calibration Verification Standard	After preparation of new calibration verification standards. Standard is from an independent.	±15 percent of expected value or within limits set by method
	Calibration Blank	Every 10 samples	<Method reporting limit
	Continuing Calibration Verification Standard	Every 10 samples	±15 percent of expected value or within limits set by method
	Method Blank	1 every 20 samples	<Method reporting limit
	MS/MSD and LCS	1 every 20 samples	Precision (%) 30 RPD Accuracy (%) 50 to 125 percent recovery Completeness (%) 90 percent recovery
	Surrogate Compound	Every sample	p-Terphenyl 33 to 141 percent recovery 2,4,6-Tribromophenol 28 to 110 percent recovery Nitrobenzene-d_5 43 to 116 percent recovery 2-Fluorobiphenyl 28 to 110 percent recovery Phenol-d_6 37 to 114 percent recovery 2-Fluorophenol 31 to 110 percent recovery
Pesticides/PCBs (Method 8080)	Calibration Curve (5 point)	At start of analysis or when continuing calibration verification standard is out of control	Per method
	Initial Calibration Verification Standard	After preparation of new calibration verification standards. Standard is from an independent.	±15 percent of expected value or within limits set by method
	Calibration Blank	Every 10 samples	<Method reporting limit
	Continuing Calibration Verification Standard	Every 10 samples	±15 percent of expected value or within limits set by method
	Method Blank	1 every 20 samples	<Method reporting limit
	MS/MSD and LCS	1 every 20 samples	Precision (%) 30 RPD Accuracy (%) 50 to 125 percent recovery Completeness (%) 90 percent recovery
	Surrogate Compound	Every sample	Tetrachloro-m-xylene or decachlorobiphenyl 20 to 147 percent recovery

TABLE B.3

LABORATORY QUALITY ASSURANCE REQUIREMENTS
SOIL AND SUMP MATERIAL ANALYSES
WASTE DISPOSAL, INC.
(Continued)

PARAMETER GROUP	CALIBRATION METHOD	CALIBRATION/QC SAMPLING FREQUENCY	ACCEPTANCE CRITERIA
Petroleum Hydrocarbons (ASTM D-2287)	Calibration Curve (5 point)	At start of analysis or when continuing calibration verification standard is out of control	Per method
	Initial Calibration Verification Standard	After preparation of new calibration verification standards. Standard is from an independent.	±15 percent of expected value or within limits set by method
	Calibration Blank	Every 10 samples	<Method reporting limit
	Continuing Calibration Verification Standard	Every 10 samples	±15 percent of expected value or within limits set by method
	Method Blank	1 every 20 samples	<Method reporting limit
	MS/MSD and LCS	1 every 20 samples	Precision (%) 30 RPD Accuracy (%) 40 to 140 percent recovery Completeness (%) 90 percent recovery

94-256 (Rpts/RdInAcWo/Rev. 2.0-11/13) (11/17/97/mc)

NOTE: MS = Matrix Spike; MSD = Matrix Spike Duplicate; LCS = Laboratory Control Sample.
RPD = Relative Percent Difference.

TABLE B.4

BASIC QUALITY CONTROL REQUIREMENTS FOR LEVEL 3 WASTE DISPOSAL, INC.

EPA LEVEL 3 QC REQUIREMENTS
• Laboratory Audit • PE Sample[(1)] • QA Plan Review • Use EPA-approved Methods[(2)] • Monthly Review • 10% Field Duplicates • Review of Final Data

94-256 (Rpts/RdInAcWo/Rev2.0/AppB)(11/17/97/cl)

(1) PE = Performance Evaluation Samples.
(2) Includes methods from SW-846.

ATTACHMENT B.1

QUALITY ASSURANCE/QUALITY CONTROL DOCUMENTATION
BY SELECTED CONTRACT LABORATORY(TO BE INCLUDED UPON
FINAL SELECTION OF ANALYTICAL LABORATORY)
(TO BE SUBMITTED AT A LATER DATE)

ATTACHMENT B.2

ANALYTICAL PROCEDURES OF SELECTED CONTRACT LABORATORY (TO BE INCLUDED UPON FINAL SELECTION OF ANALYTICAL LABORATORY)
(TO BE SUBMITTED AT A LATER DATE)

APPENDIX B.3

SOP O

METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and intemal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤ 2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

<u>NOTE</u>: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are <u>known</u> to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample <u>not</u> preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is <u>known</u> to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is <u>not</u> known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or, 7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is not preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 μg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

10.0 REFERENCES

1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., "Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil", Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., "Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods", Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., "Soil Sampling and Analysis for Volatile Organic Compounds", Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., "Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate", SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil", Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., "Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry", Hydrocarbon Contaminated Soils, 1993, 3; 135-45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., "Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out", 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., "Comparison of Analytical Methods for Determination of Volatile Organic Compounds", Envir Sci Tech, 1992; 26; 1932-8.

TABLE 1

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

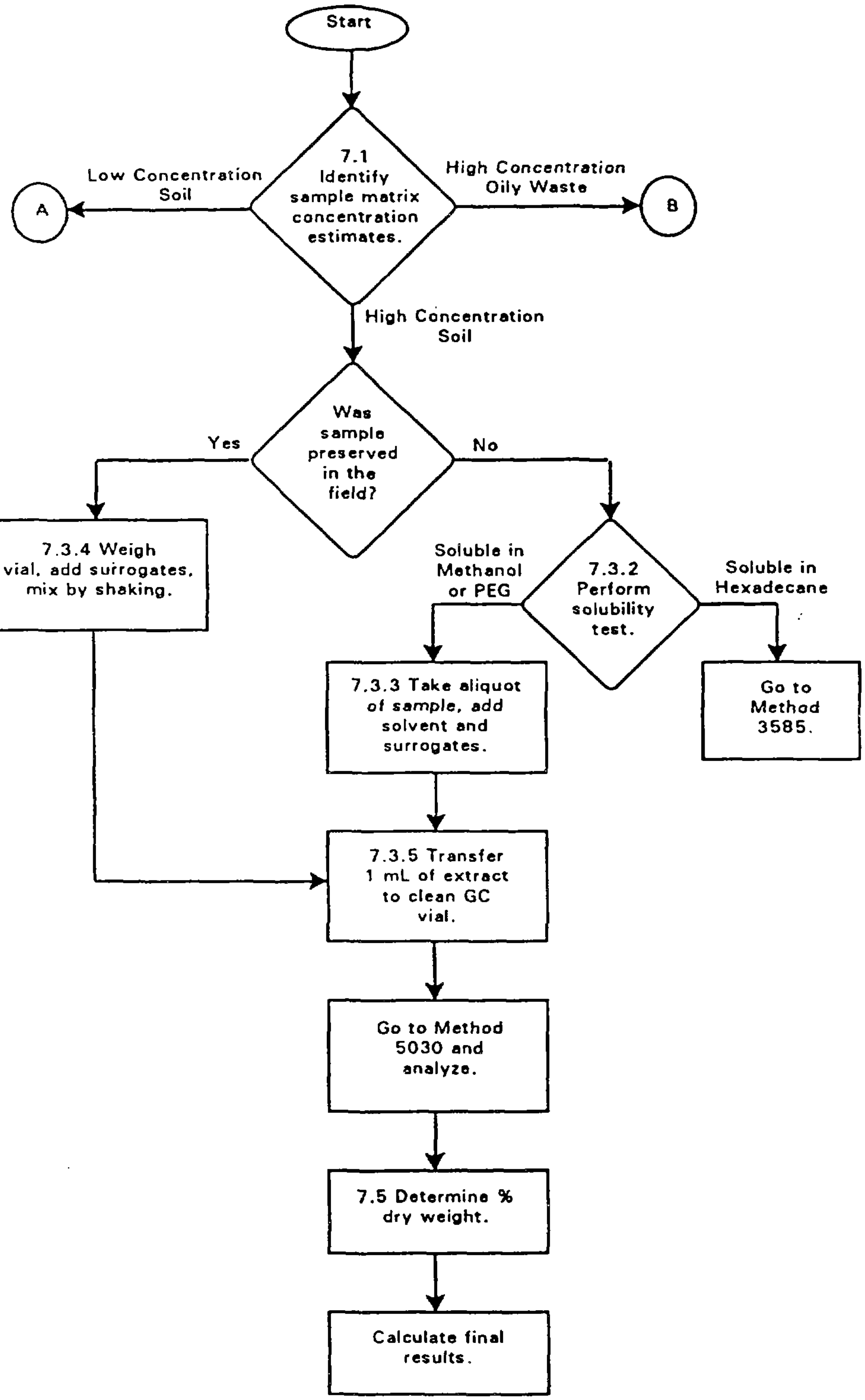
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

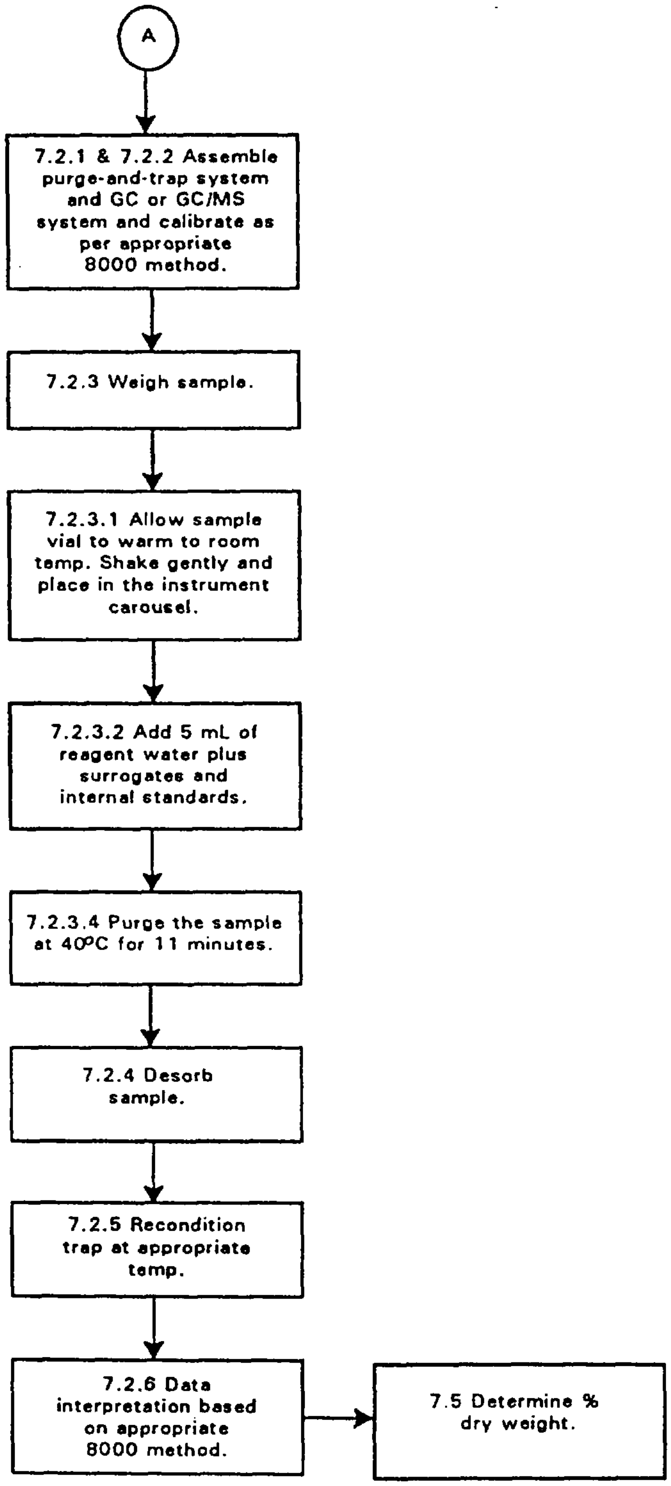
Calculate appropriate dilution factor for concentrations exceeding those in this table.

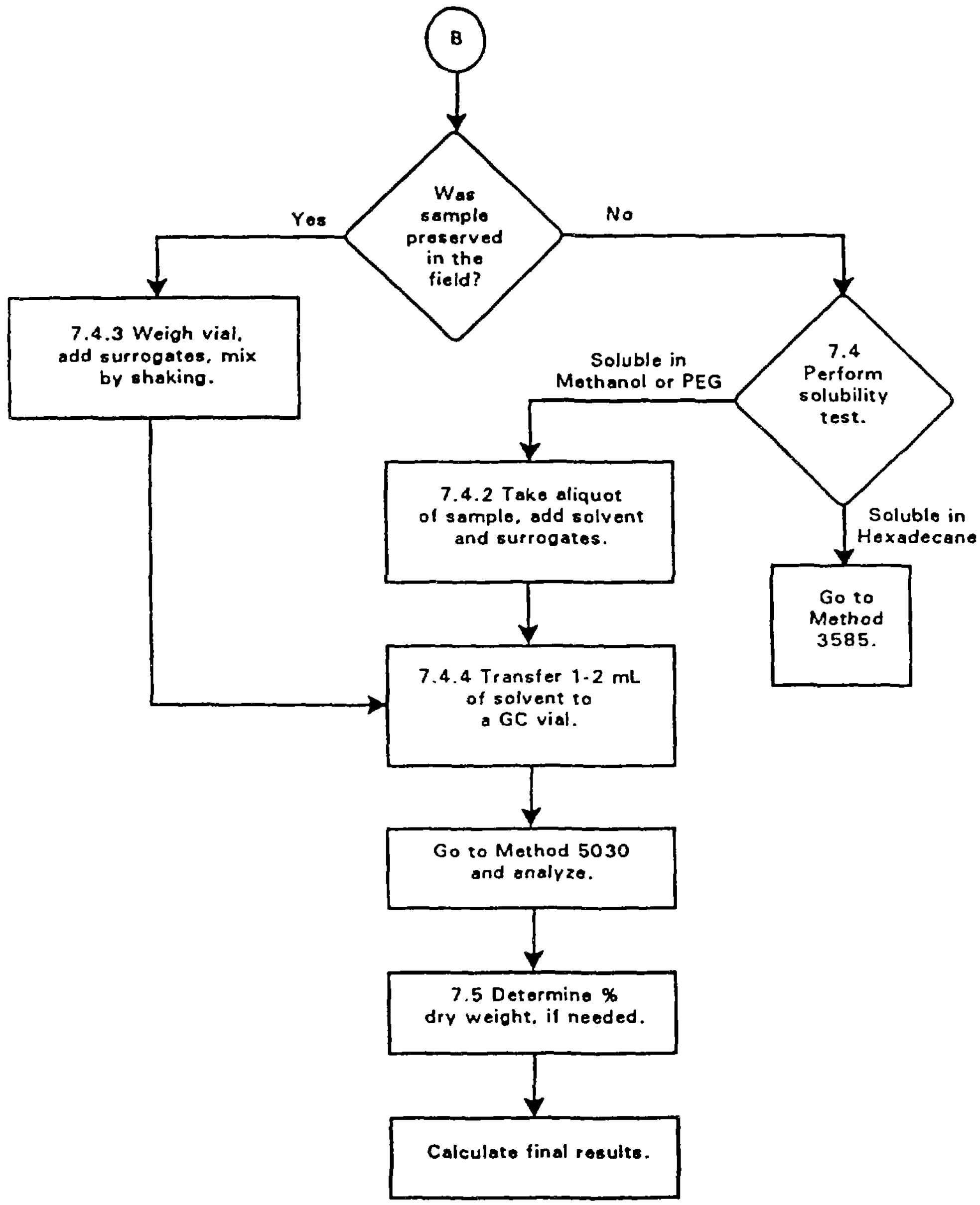
[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

METHOD 5035
CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION
FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES




A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.